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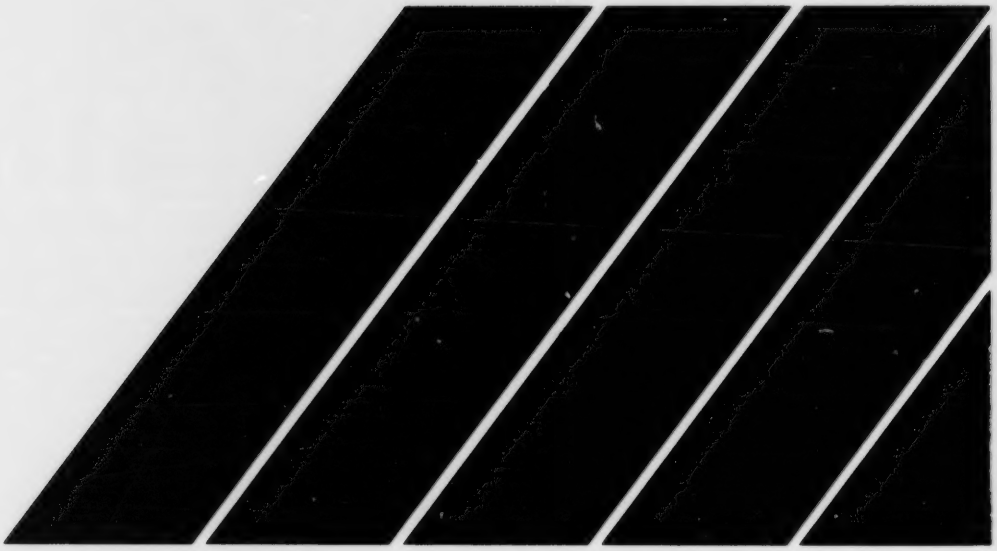
DEVELOPMENT OF PROTOTYPE ALL-SOLID SMART WINDOW DEVICES
(December, 1987 to March, 1990)



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DEVELOPMENT OF PROTOTYPE ALL-SOLID SMART WINDOW DEVICES
(December, 1987 to March, 1990)

PREPARED FOR:

Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
Ottawa, Ont.
DSS Contract No. 23283-7-6207/01-SS
June, 1990

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183AP

MICROMEDIA

91-01215/

CITATION

Dao, L.H., INRS-Énergie. Development of Prototype All-Solid Smart Window Devices (December, 1987 to March, 1990). DSS Contract No. 23283-7-6207/01-SS. Efficiency and Alternative Energy Technology Branch, Energy, Mines and Resources Canada, Ottawa, Ontario. 1990 (94 pp.)

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Catalogue No. M91-7/98-1990E
ISBN. 0-662-18036-4

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SUMMARY

The purposes of this report are to summarize the research and development of the electrochromic (EC) windows at INRS-Energie, to summarize the fundamental research that led to the uniqueness of our devices and to recommend the design for an advanced EC windows for buildings applications.

After a brief overview of the current state-of-the-art on EC windows, the design of an all solid-state complementary EC window structure, the evaluation criteria determining the performance and the durability of candidate EC device are reviewed. The recent progresses on new EC materials and solid electrolytes developed at INRS-Energie are presented.

The main technique used for thin films coating at INRS-Energie is electrochemical deposition. Our approach is unique in the world. It permits us to cover large surface of glass with an inexpensive technique.

The performance criteria are described. Performance evaluation based on optical and electrochemical properties, and spectroelectrochemistry are summarized. Durability tests are also recapitulated.

The performance and the durability of four all solid-state complementary EC window prototypes are discussed in detail. These include measuring the transmittance in the coloured and bleached states, the long term cyclability, the response time and the memory effect.

For the conclusion, a set of recommendations is made for advancing EC window technology.

RESUME

L'objet de ce rapport est de résumer la recherche et le développement sur les fenêtres électrochromiques (EC) effectués à l'INRS-Energie, la recherche fondamentale qui a conduit à la construction originale des unités EC, et de recommander le design d'une fenêtre électrochromique avancée pour les batiments.

Après un court aperçu de l'état actuel des connaissances sur les fenêtres électrochromiques et de la conception d'une fenêtre EC complémentaire tout-état-solide, les critères d'évaluation des performances et de durabilité des unités EC sont indiquées. Les progrès récents sur les nouveaux matériaux EC et les électrolytes solides développés à l'INRS-Energie sont présentés.

La technique de préparation de films minces principalement développée à l'INRS-Energie dans le cadre de ce projet est la déposition électrochimique. Cette approche qui est unique au monde, permet de recouvrir de large surface avec une technique relativement bon marché.

Les critères de performance sont décrites. L'évaluation des performances basée sur les propriétés optiques et électrochimiques et la spectrochimie est résumée. Les tests de durabilité sont aussi récapitulés.

La performance et la durabilité de quatre prototypes de fenêtres EC complémentaires sont présentées en détail, en particulier les mesures de transmittance

à l'état coloré et à l'état transparent, de la cyclabilité à long terme, du temps de réponse et de l'effet de mémoire.

Comme conclusion, nous présentons une série de recommandation pour développer la technologie des fenêtres EC avancées.

PREFACE

The project "Electrochromic Materials and Polymers Electrolytes" is divided into two separate sub-projects: the fundamental research and the development of prototypes.

For the fundamental research sub-project, funded by NSERC (operating, strategic and equipment grants) and INRS-Energie (post-doctoral fellowships and graduate scholarships), we have prepared new electrochromic materials and new solid polymer electrolytes by innovative and economical deposition techniques. Their optical, electrical electrochemical and electrochromic properties have been studied.

Some specifically identified candidate materials have been then investigated in the development sub-project, funded by EMR of Canada (contracts), for the fabrication of prototype smart window devices. Problems encountered in this part were fed back to the fundamental research team for solution.

The success of this project is made possible by the hard work and dedication of my collaborators (professor, post-docs, graduate students, research assistants and technicians), members of the Laboratoire de Recherche sur les Matériaux Avancés at INRS-Energie.

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INTRODUCTION

The purpose of this report is to summarize the recent progress in the development of new electrochromic materials and solid-state polymer electrolytes at INRS-Energie, the uniqueness of our approach (thin film deposition technique) to develop an efficient and stable EC device compared with the world current state-of-the-art, and to describe the all solid-state complementary EC window laboratory prototypes for building applications.

The objectives of this report are to present a background about complementary EC window devices and to show why this design is better than other approaches. Our laboratory is well known for the development of new EC materials, particularly EC conducting polymers and of new thin films coating techniques.

We then present the performance and durability of four all solid-state EC laboratory prototypes with different polymer electrolytes.

And to conclude, we make recommendations for advancing the state-of-art beyond the laboratory stages through the prototype and commercial product stages.

A number of technology areas have been identified where EC devices have some clear applications potential. One important potential application for solid-state thin film electrochromic materials is "smart" windows. "Smart" windows can be used to improve the energy efficiency of buildings by electrically controlling the radiant energy transfer through them. Reflection modulation is desirable for such application for two main reasons: 1) to avoid excessive strain and degradation due to heat produced by optical absorption; and 2) to avoid a decrease in thermal efficiency associated with the radiative emission arising from heat producing optical absorption. Other applications include eyeglasses, displays, aerospace and vehicles uses.

The US window glass production is about four billion square feet per year for building, with about 700 million square feet used in sealed insulating windows. For Canada, the figure is approximately one tenth.

Although no figure on energy saving is calculated for switching window, some estimates indicated that several kWh/ft^2 per year could be saved by the use of a well programmed, automatically control, switchable window in commercial and residential building. The energy savings potential could be tremendous.

EC windows, besides a net energy benefit, are also providing design options for commercial builders, and for interior architects and designers.

At the present state of the art, technological development of an EC window is still a high-risk project for industry (except in Japan), but they are strongly supported by governments (in Canada by EMR). The ultimate acceptance will depend on the demonstration of technical and economic feasibility.

Therefore, our efforts have been oriented towards the development of the ideal multilayer solid-state electrochromic window structure as shown in Figure 1. Our EC window device is based on aesthetically, inexpensive materials and on cost-effective fabrication processes with high potential for economic scale-up.

We have demonstrate the technical feasibility of our EC window laboratory prototype. We are confident that our approach is one of the most cost-effective one and depending on further development, our design has the potential for economic scale-up and long term stability, besides functionality and aesthetically pleasing.

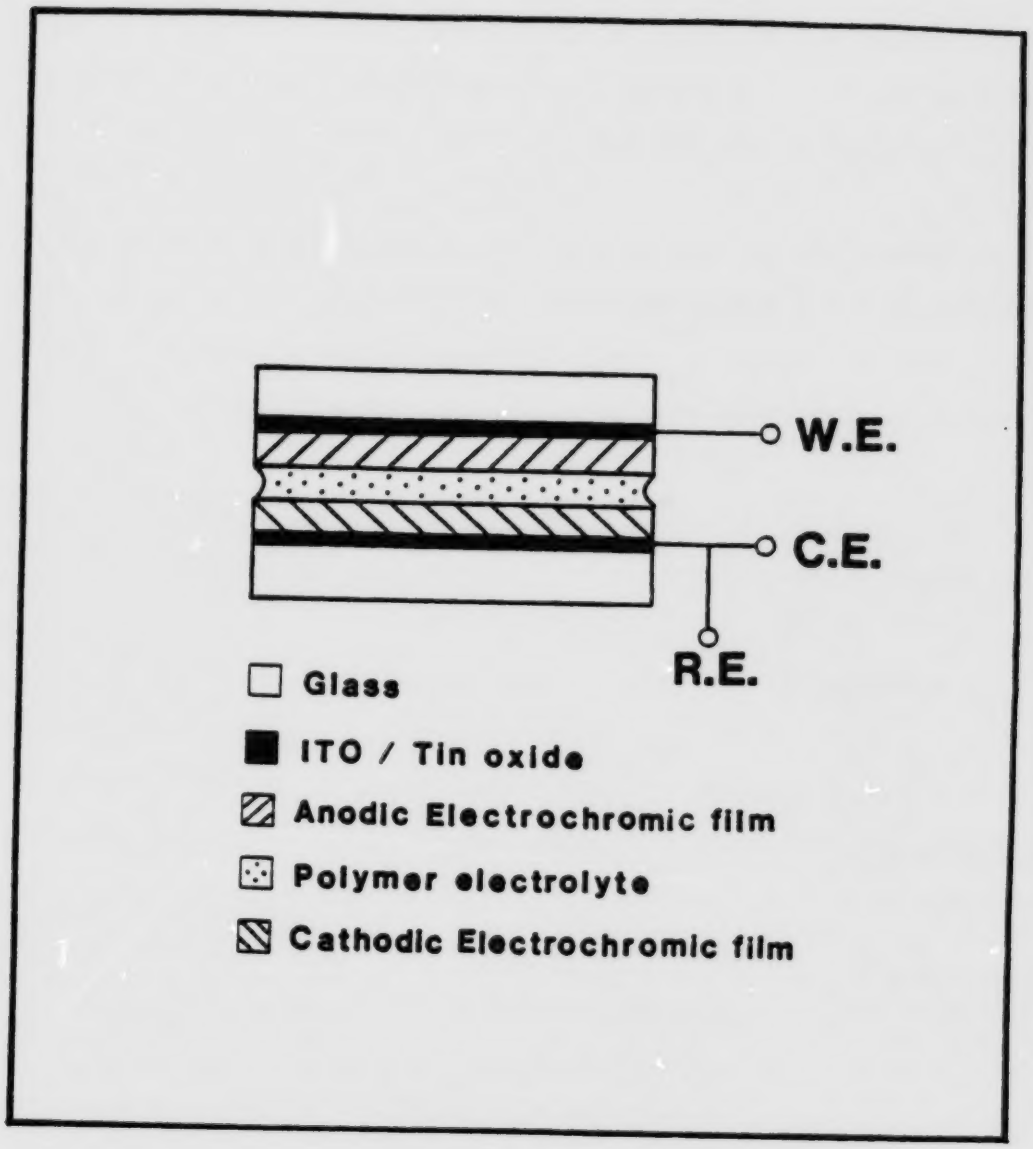


Figure 1. Structure of a complementary EC window.

BACKGROUND

AND

ELECTROCHROMIC SMART WINDOW STRUCTURE

2.1. BACKGROUND.

Recently, there are considerable attractions in the research and development of materials and devices for optical control of large scale glazings. Among several potential switching technologies considered for glazing, e.g. liquid crystals, photochromism, solvochromism, thermochromism and electrochromism; electrochromism is considered as one of the most promising technologies for optical switching control. In contrast to the other technologies, the optical properties of EC windows can be control at will, and the power required to drive the device and to maintain the given optical states (bleached or coloured) is minimal.

Electrochromic "smart" windows are prospective devices for the control of light transmission in response to the change in brightness of the environment. The basic structure of such a window or electrochromic cell is comprised of three types of thin film materials: a) transparent electrical conductors TEC (e.g. ITO, Nesa) on glass or plastic supports to collect the current, b) electrochromic EC layer films on TEC to form the opto-electroactive elements of the window and c) an ionically conductive electrolyte IC to separate the two EC films. A schematic of a complementary EC window is shown in Figure 1.

Although EC windows have great potential for commercial applications, they have, as all new technologies, a large share of problems and uncertainties. Degradative effects are still the major barriers for many different devices, e.g. residual coloration, loss of dynamic range, loss of stability and reversibility during long term cycling and large temperature range. The origins of the effects are only partially understood because of the lack of fundamental research.

A large variety of materials are known to display electrochromism. They may be divided into five general classes : a) transition-metal oxides, b) conducting polymers, c) organic, d) intercalated and e) others materials. The bulk of the research published to date have been related to transition-metal oxides (e.g. $W0_3$, MoO_3, IrO_2 etc.), although many works have been carried out recently on conducting polymers.

Another major problem in the present EC window technology is the lack of efficient electrolyte. Both inorganic and organic (polymeric) solid electrolytes were considered, taking account not only their optical and physical properties but also the economics of manufacturing and long term durability of the devices. Until now, no performing electrolytes have been developed.

Large surface EC windows will experience extreme temperature and pressure fluctuations when used in a configuration for control of solar gain, particularly in a country like Canada. Experiences gained in the development of super-window technologies will be surely profitable.

2.2. STRUCTURE OF A COMPLEMENTARY E.C. WINDOW.

Many electrochromic cells reported in the literature are lacking one or more of the basic components described in Figure 1, resulting in poor long term stability and cyclability. Complementary electrochromic windows, based on cathodically colouring WO_3 and anodically colouring IrO_2 or polyaniline, have been fabricated. However, their development is still limited by hight costs of fabrication (vacuum evaporation, sputtering), prohibitive costs of materials (IrO_2) and short term stability of materials (polyaniline).

A complementary electrochromic window device is based on a combination of a cathodic electrochromic electrode and an anodic electrochromic electrode separated by a solid electrolyte. The operation of the electrochromic device is such that both layers participate in the colouring and bleaching processes, therefore enhancing the overall efficiency of optical switching. For example, the electrochromic reactions occurring in tungsten oxide cathode and poly(aniline) anode during optical switching are shown in Scheme I.

SCHEME I

cathodic

$$WO_3 + xM^+ + xe^- \rightleftharpoons M_xWO_3$$

anodic

transparent **blue**

anodic

$$Poly(An) + xA^- - xe^- \rightleftharpoons Poly(An)A_x$$

cathodic

pale yellow **blue**

WO_3 film undergoes a transparent to blue modulation on the electrochemical insertion (colouring) or ejection (bleaching) of a cation M^+, typically H^+, Li^+ or Na^+. In the same time, poly(An) modulated between pale yellow to blue on the electrochemical injection (colouring) or extraction (bleaching) of an anion A^-, typically ClO_4^-, $CF_3SO_3^-$. When the direction of the current flow in tungsten oxide poly(aniline) electrochromic device is such that the tungsten oxide layer is the cathode and poly(aniline) layer the anode, a dual injection of M^+ in WO_3 and A^- in poly(An) takes place and the electrochromic device develops a deep blue coloration. When the direction of current flow is reversed, the cation and anion are ejected from the electrochromic layers **EC** to the electrolyte reservoir. The electrochromic device returns then to the transparent state (Figure 2).

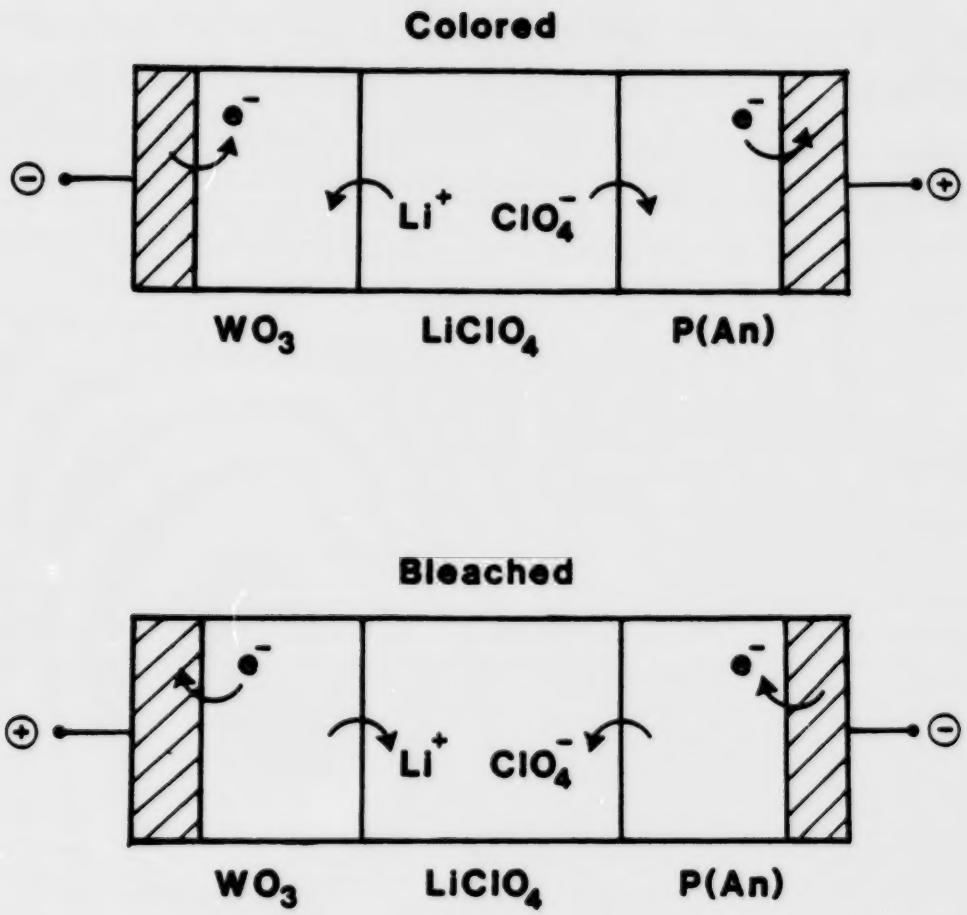


Figure 2. Bleaching and coloration mechanism.

CRITERIA FOR E.C. WINDOWS

There are a large number of parameters which are usually divided in evaluation criteria, performance criteria and testing methods. Evaluation criteria include those parameters influencing commercial feasibility such as parameters for ranking the materials used in each component layer and for a complete EC device. Performance criteria deal with the physical properties of EC devices.

3.1. EVALUATION CRITERIA.

Usually the criteria for evaluating EC windows are divided in two categories: 1) criteria for ranking candidate materials used in the devices, i.e the electrochromic layers, the transparent conductive layer, the ionic conducting layer etc., and 2) criteria for complete EC windows.

Each layer is chosen based on its desired properties, then optimized to yield the required optical properties, the expected durability and functionality. Usually the deposition techniques are very important for the EC device development, because they influence the coating structure, morphology, composition and properties. Each technique must be analyzed in relation to capital investment, process cost, materials compatibility and films properties.

There are a number of criteria such as 1) designed function, 2) aesthetically acceptable, 3) economic, 4) minimum performance expectations, 5) durability and 6) system analysis, to take in consideration when ranking a complete EC window device. For detail, consult reference. An example of performance criteria is shown in Table 1.

TABLE 1. Performance Criteria for EC Windows.

SPECTRAL RESPONSE	
Solar control	T_s (bleached) = 50-70%
	T_s (coloured) = 10-20%
Visible control	T_p (bleached) = 50-70%
	T_p (coloured) = <10-20%
NEAR-IR CONTROL	
Reflective device	R_{nir} (bleached) = 10-20%
	R_{nir} (coloured) = >70%
SWITCHING VOLTAGE	1-3 Volts (small device)
	10-24 Volts (large device)
MEMORY	1-12 Hours
CYCLING LIFETIME	$>10^3$-10^6 Cycles
LIFETIME	5-20 Years
OPERATING TEMPERATURE	-30 to 70 °C
	0-70 °C, if protected

3.2. PERFORMANCE CRITERIA.

Usually, the performance of an EC device is based on the following performance criteria:

. optical properties,

. ion insertion, colour centres, injected charge,

. open circuit memory

. energy cycle

. response time

. substrate effects

. temperature effects

All these criteria must be answered and optimized before any durability testing.

3.3. STABILITY AND DURABILITY OF EC WINDOWS.

In order to realise all the potential of EC windows, problems related with degradation must be solved. The mechanisms, effects, modes of degradation must be understand and solve. After that, performance measurements for real time and accelerated testing must be completed to establish all aspects of any performance losses by the device.

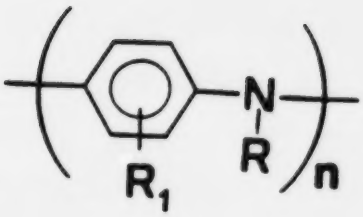
RECENT PROGRESS
ON
NEW MATERIALS
DEVELOPED
AT
INRS-ENERGIE

4.1. ELECTROCHROMIC LAYER EC (ANODE).

Electropolymerized polyaniline films have received considerable attention owing to their opto-electrical properties and potential applications. The electrochromic properties of polyaniline films have been studied for display devices applications. It has been reported that an electropolymerized polyaniline film showed reversible multiple colour changes from transparent yellow at -0.2 V vs SCE to green at 0.5, dark blue at 0.8 and black at 1.0. Since polyaniline deteriorated upon exposure to potentials higher than 0.6 V in acidic aqueous solution, it is necessary to lower the upper limit potential as much as possible (to 0.4 V, green colour) to get durable repetitive cycles but at the expense of colour range and contrast. Therefore, it is necessary to develop new materials with better opto-electrical properties. It is known, in polymer sciences, that the incorporation of substituents in the backbone of a polymer can change its properties. Our interests in solid-state batteries and electrochromic devices led us to investigate the electrochemical and chemical polymerization of several aromatic ring and nitrogen substituted aniline derivatives.

For aniline and diphenylamine, different substituents can be attached to the nitrogen and the ortho and meta position of the aromatic ring. Because the preferential head-to-tail polymerization mechanism, only anilines with aryl substituents on position para can be polymerized as shown in Scheme II.

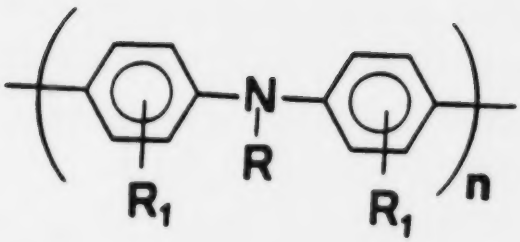
SCHEME II



R = H, C_1... C_{12}

R_1 = H, Me, Et

Poly(aniline)



R = H, C_1... C_6

R_1 = H, Me

Poly(diarylamine)

Polyaniline and diphenylamine derivatives with substituents on the aromatic ring or on the nitrogen were prepared by chemical or electrochemical polymerization (Scheme II). Uniform and stable thin films showing good and stable electrochromic properties were deposited on transparent conducting electrodes directly by electropolymerization or from solution casting. No significant modification in the cyclic voltammograms were observed after thousand cycles in aqueous acid solution or in acetonitrile. Upon cycling between the potential limits (first and second oxidations peaks), most of poly(aniline) derivatives films show multiple and reversible colors changes from pale yellow to dark blue. Among the electrochromic anodic materials (see appendix), two best candidates - poly(diphenylamine) **Poly(DPA)** and poly(N-benzylaniline) **Poly(BAn)**- were selected and used in the prototype smart window devices.

The detail of the preparation, characterization and properties of the anodic electrochromic polymer layer can be found in the reprints No. 1, 2 and 3 (appendix). Usually, the electropolymerization was performed in a one-compartment cell equipped with an ITO glass plate and a nickel foil as working and auxiliary electrodes, and a Ag/AgCl 3.8 M KCl reference electrode. Oxidative deposition of polymer films was obtained from solutions containing 0.1 M of monomer (e.g. diphenylamine, N-phenylnaphthylamine) and 1.0 M of lithium perchlorate. Uniform polymer films were obtained by applying a constant potential of 0.80 and 0.65 V for diphenylamine and N-phenyl-1-naphthylamine respectively. The films were then washed with acetonitrile in an ultrasonic bath to remove the oligomers and the excess of monomer.

4.1.1. Poly(diarylamines)

Figure 3 shows cyclic voltammograms of the poly(N-naphthylaniline) film (1.6 μm thick) in a 1 M $LiClO_4$-CH_3CN solution after 1 scan (curve a) and 200 scans (curve b). One broad and symmetrical oxidation peak is observed at 0.73 V which is only 0.03 V lower than the monomer oxidation potential (0.76 V). This feature can be explained by the weak electronic delocalization in the polymer chain due to a non-planar conformation between phenyl and naphthyl groups. In effect, it was showed that N-arylanilines polymerized, not by a head-to-tail mechanism as observed for polyaniline, but by a 4-4' coupling mechanism implying the insertion of the aryl group in the polymer backbone. Only a small change in the current intensity was observed in the voltammogram shape after more than two hundred potentials cycles between 0.3 and 1.0 V. The good cyclability of the poly(N-naphthylaniline) film is probably due to the highly porous structure of the polymer which provides a large contact surface with the electrolyte and efficient self-exchanges of electrons.

The polymer film on ITO exhibits multiple colour changes (yellow-red-purple-dark blue) when the potential is cycled between 0.0 and 0.8 V vs. Ag/AgCl as shown in the absorption spectra (Figure 4). At 0.0 V ,the yellow film in the reduced form presents a visible absorption spectrum with only one absorption band at 382 nm . This absorption peak can be related to the transition between the valence and the conduction bands and hence to the band gap. When the applied potential is increased to 0.6 V, the polymer film turns red with a new absorption band at 540 nm. At 0.7 V, the polymer film becomes purple and this is followed by a simultaneous increase and widening of the 540 nm band. A dark blue colour film is obtained when the potential reaches 0.8 V and the spectrum shows a broad band that covers practically the whole visible spectral range. Concurrent with these modifications, the 382 nm band decreases in intensity and shifts

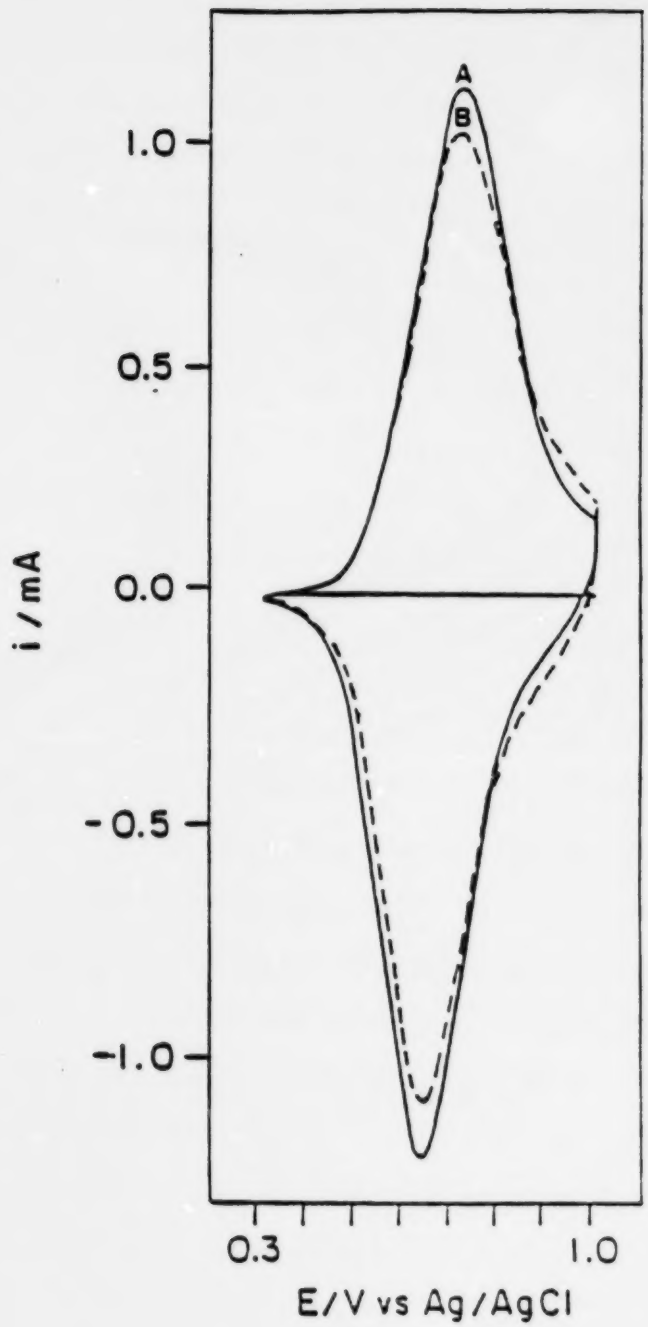


Figure 3. Cyclic voltammogram of poly(N-naphthylamine) film on ITO in acetonitrile.

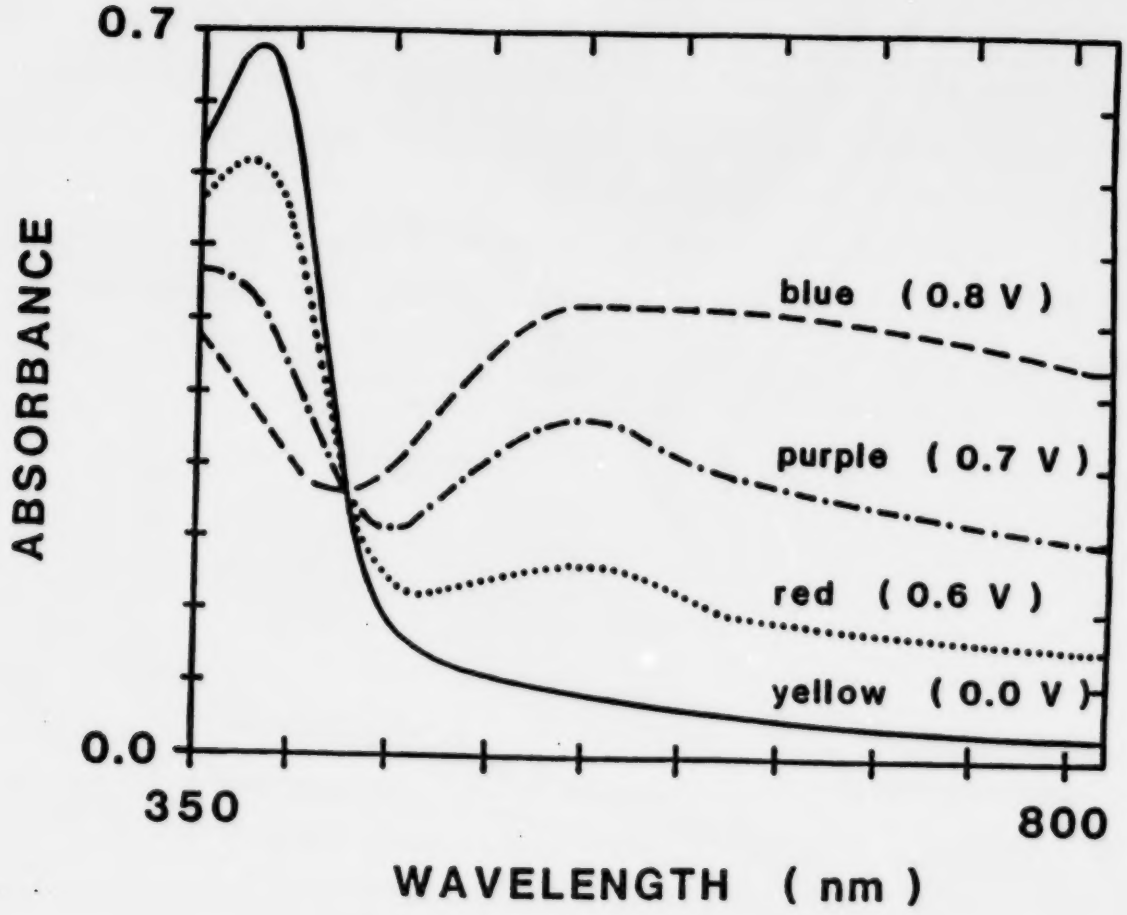


Figure 4. **Spectroelectrochemistry of poly(N-naphthylamine) film on ITO in acetonitrile.**

to higher energies. These new peaks in the visible region can be related to the formation of polarons. The most striking point is in the fact that all colours from yellow to dark blue are reversibly obtained in the very small range of only 0.3 V between 0.5 and 0.8 V vs. Ag/AgCl, corresponding to the single peak observed in cyclic voltammetry (Figure 3). As far as we know, this phenomenon is unique for conducting polymers. Poly(aniline) also exhibits multiple colour changes (pale yellow - green - dark blue) over a large potential range between -0.2 and 0.8 V vs. SCE, but irreversible degradation occurs when the potential is raised above 0.6 V.

Figure 5 displays the cyclic voltammogram of a poly(diphenylamine) film in a 1 M $LiCLO_4$-acetonitrite solution. Two oxidation peaks are observed at 0.55 and 0.83 V, corresponding probably to the oxidation of aromatic polyamine for the first peak, and to the oxidation of quinoid polyimine for the second. Electrical measurements by the four-probe technique of a pressed pellet indicated a room temperature conductivity of ca 2 $S.cm^{-1}$. The polymer film shows multiple colour changes (clear yellow - yellow - brown - blue) when the potential is cycled between 0.0 and 1.0 V vs. Ag/AgCl (Figure 6). At 0.0 V, the clear yellow film in the reduced form presents a visible absorption spectrum with a peak at 350 nm and a shoulder at 380 nm. When a potential of 0.6 V is applied, the film turns to yellow with a new absorption at 460 nm. The film turns green at 0.8 V. A green-blue film is obtained at 1.2 V, and the spectrum shows a broad band covering the whole visible spectral range.

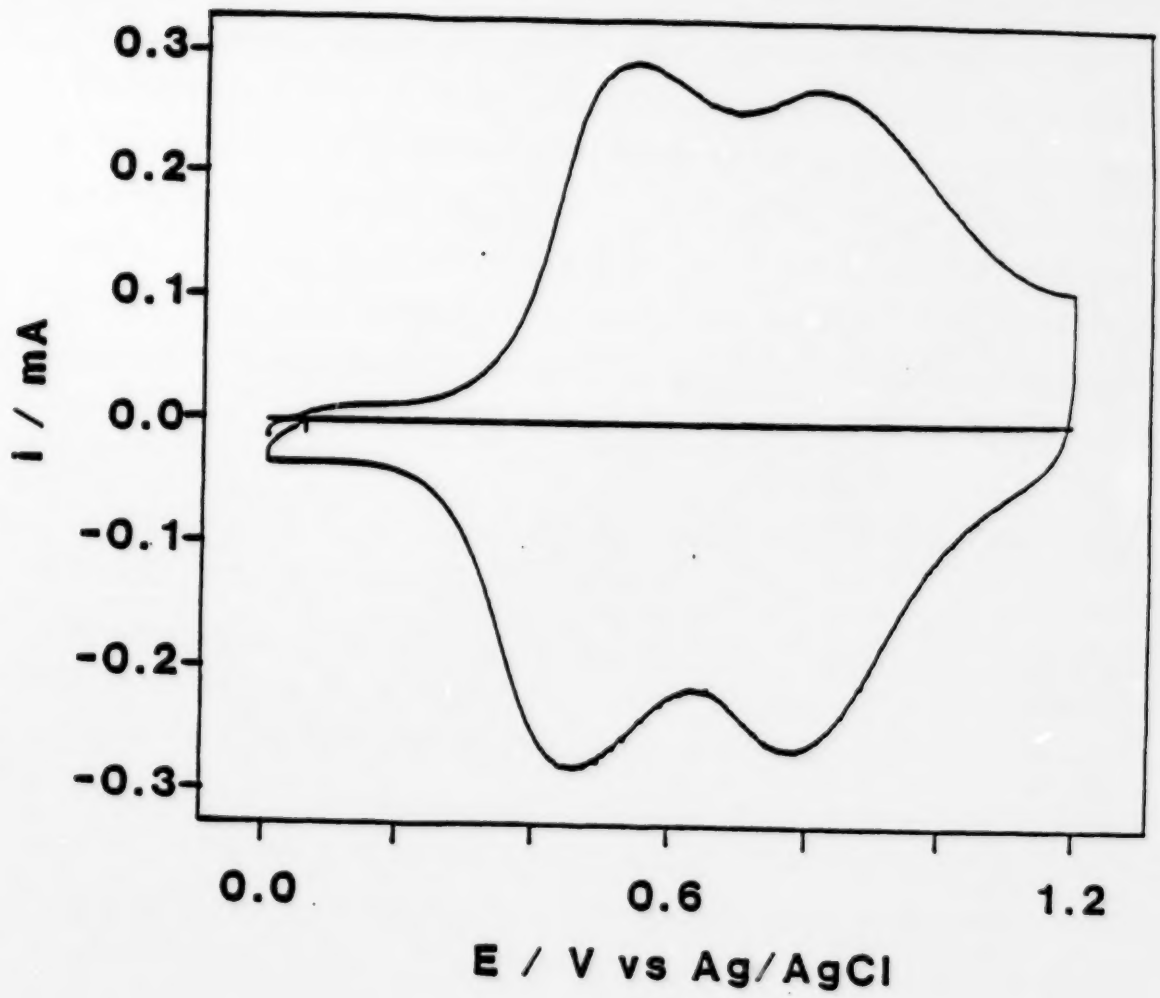


Figure 5. Cyclic voltammogram of poly(diphenylamine) film on ITO in acetonitrile.

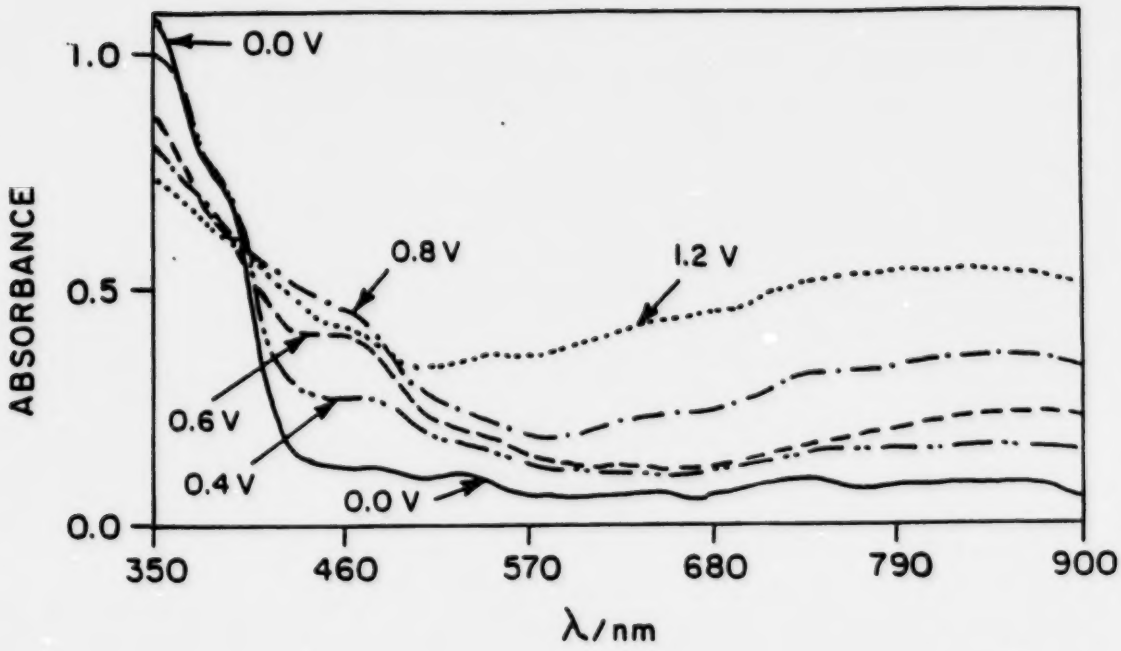


Figure 6. Spectroelectrochemistry of poly(diphenylamine) film on ITO in acetonitrile.

4.1.2. Poly(N-benzylaniline)

Figure 7 shows cyclic voltammograms of a poly (N-benzylaniline) thin film casted from an acetonitrile solution onto an ITO coated glass electrode in 1.0 M aqueous perchloric acid solution between 0.0 and 0.9 V at four different scanning rates. Thin films of **PBA** prepared by electropolymerization directly on ITO glass present similar voltammograms shapes. As observed for others poly(anilines), two oxidation peaks are observed at 0.3 and 0.6 V, corresponding probably to the formation of polarons and bipolarons. The most noticeable observation concerns the absence of the degradation peak currently reported for the polyaniline. The polymer film also shows a relative stability over a thousand scans in perchloric acid 1.0 M.

The polymer films on ITO exhibit multiple colour changes (colourless-yellow-green-blue) when the potentials were cycled between 0.0 and 0.8 V vs Ag/AgCl as shown in the absorption spectra (Figure 8). Figure 8A corresponds to the electropolymerized film on ITO glass and Figure 8B corresponds to a solution-cast polymer film from an acetonitrile solution. At 0.1 V, no significant absorption was observed at 700-800 nm while a relatively strong absorbance peak was present at 430 nm corresponding to the reductive state of the polymer which is almost colourless. At higher potential, 0.3-0.4 Volt, the polymer becomes yellow and the absorbance band at 700-800 nm increases as well as the one at 400 nm. At 0.6-0.7 V, the polymer film becomes green as denoted by a very strong absorbance peak in the 700-800 nm region. Finally, at 0.8 V the colour of the film becomes blue while the spectrum shows an increasing absorption band in the 500-600 nm region.

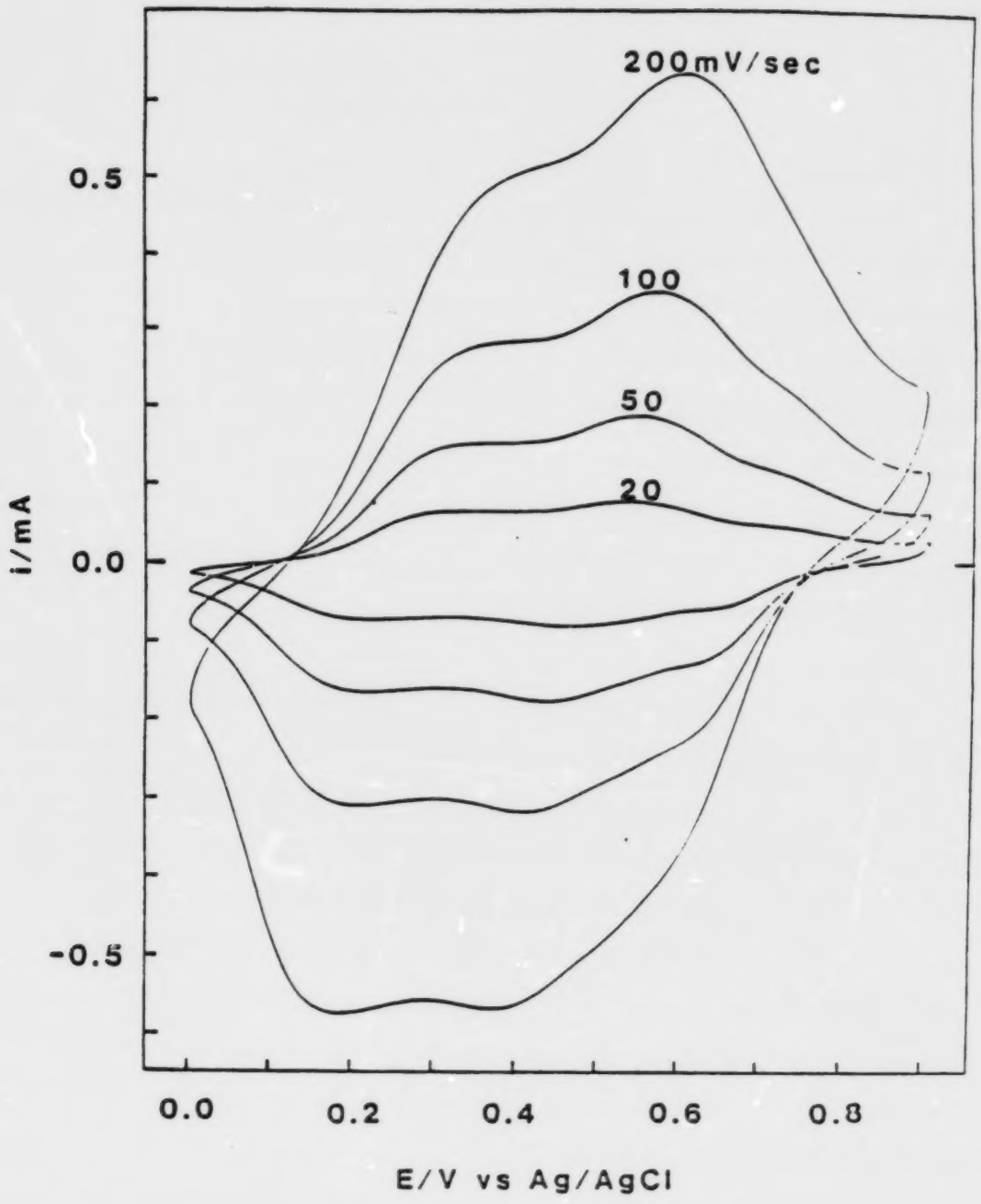


Figure 7. **Cyclic voltammograms of poly(N-benzylaniline) film on ITO in perchloric acid.**

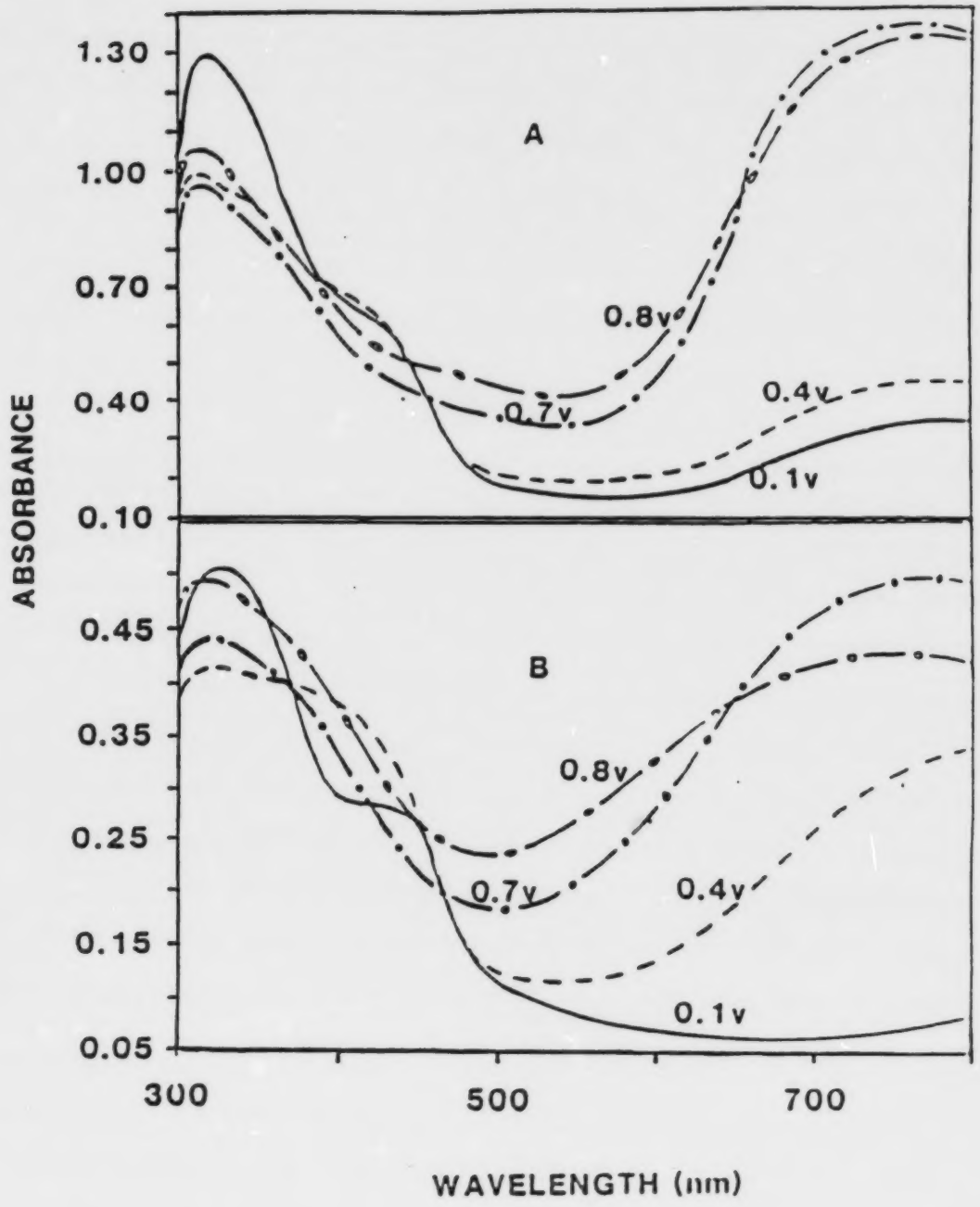


Figure 8. **Spectroelectrochemistry of poly(N-benzylaniline) film on ITO in perchloric acid.**

The molecular weights of the perchlorate-doped polymer were investigated by Gel Permeation Chromatography. The THF soluble fraction of the chemically prepared **PBA** shown an average molecular weight of 25,000 which denotes a high degree of polymerization, while the electrochemically prepared polymer presented a lower average molecular weight (5,000). Similar results were observed with poly(alkylanilines).

4.1.3. Conclusion

In summary, we have prepared many new derivatives of polyaniline which present very interesting optical, electrical and electrochemical properties. Uniform and stable thin films showing good and stable electrochromic properties can be prepared directly by electrodeposition or from solution casting. No significant modification has been observed in the cyclic voltammogram after thousand of cycles between 0.0 V and 1.0 V vs Ag/AgCl in 1 M $LiClO_4$-acetonitrile solution. Upon cycling between these potential limits, most of pol(aniline) derivatives films show multiple and reversible colour changes from colourless to yellow to red and to dark blue. Reproducible doping and undoping by electrochemical methods has been demonstrated, suggesting potential applications of this new conductive polymer to electrochromic devices. Among these electrochromic materials, two best candidates -poly(diphenylamine) and poly(N-benzylaniline)- were selected and used in the prototype "smart" window devices.

4.2. COUNTER-ELECTRODE LAYER CE (CATHODE).

Transition-metal oxides were used in our smart window structure as counter-electrodes **CE**. Of the identified candidate materials that we have investigated are : WO_3, MoO_3, V_2O_3 and their doped derivatives. All of them are very promising. The most common method for transition-metal oxide film formation is by vacuum techniques, but other methods have also been reported. These methods include chemical vapor deposition, spin, dip coating, oxidation of metal and very recently for tungsten oxide, electrodeposition from tungsten-hydrogen peroxide solution. The deposition observed can be explained in terms of solubility differences between the peroxometallic acid and the metal oxide hydrate. We have adapted the peroxide deposition method to produce by electrodeposition, WO_3, and for the first time, MoO_3.

The detail of the preparation, characterization and properties of the transition metal oxides films can be found in the reprints 4 and 5 (appendix).

4.2.1. Tungsten Oxide

WO_3 thin films (1-3 μm) were obtained from tungsten-hydrogen peroxide solution on tin-oxide glass (30 ohm/square, 10 x 10 cm^2) in a one-comportment cell using Ni foil and Ag/AgCl (3.8 M KCl) as counter and reference electrodes, by cycling the potential between - 400 mV and - 800 mV at a scanning rate of 60 mV/s. Pulsed plating electrodeposition was also successfully used and high quality films were obtained. The deep blue films were extensively rinsed with water and then thermally treated for one hour at 130 ^{0}C. The electrochemical properties of the deposited WO_3 films were studied in

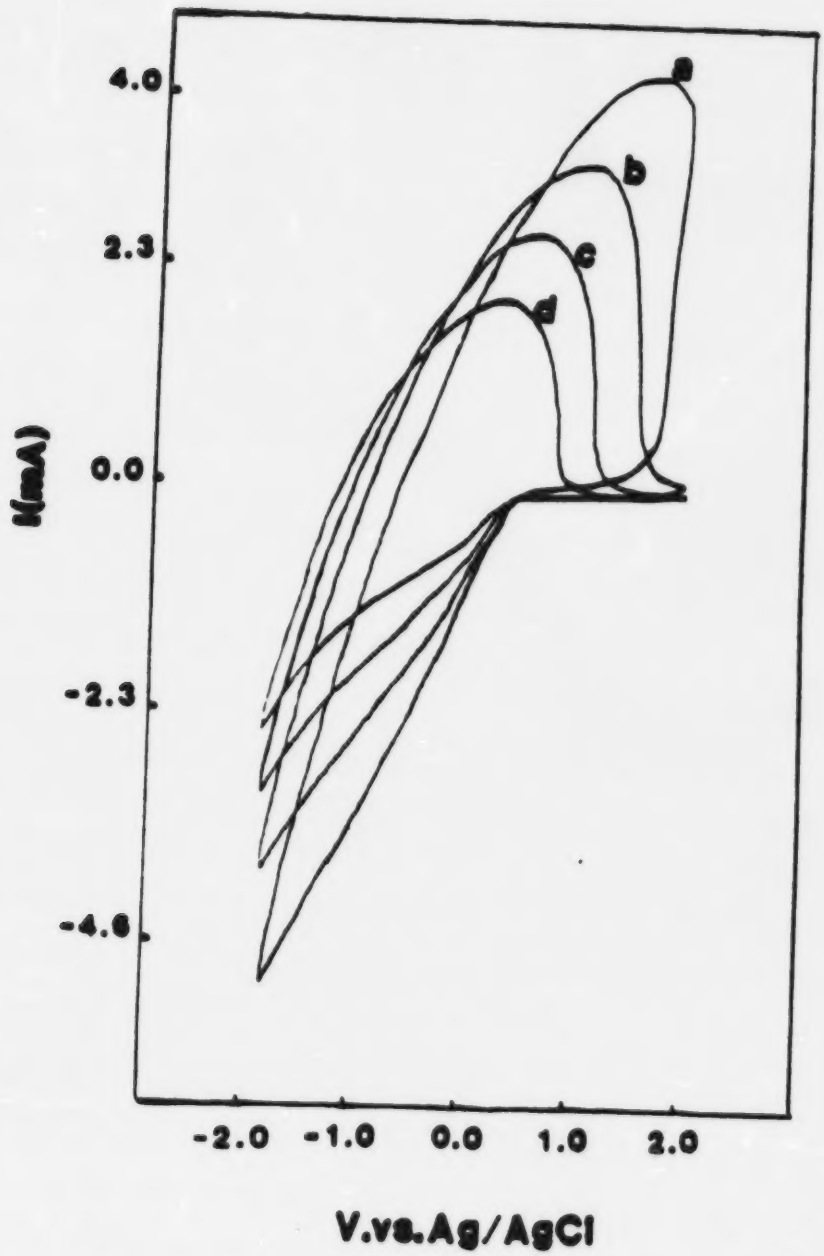


Figure 9. **Cyclic voltammograms of tungsten oxide film on ITO prepared by d.c. electrodeposition**

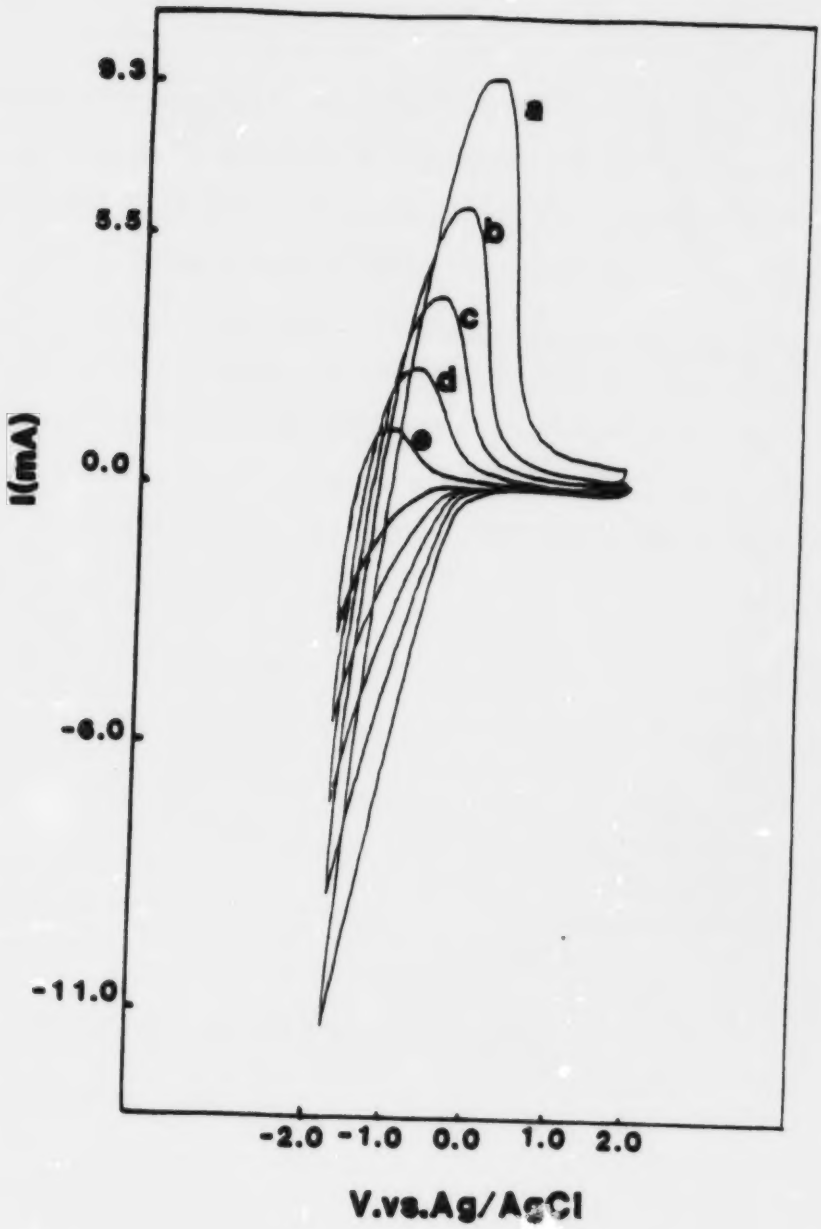


Figure 10. Cyclic voltammograms of tungsten oxide film prepared by pulse plating.

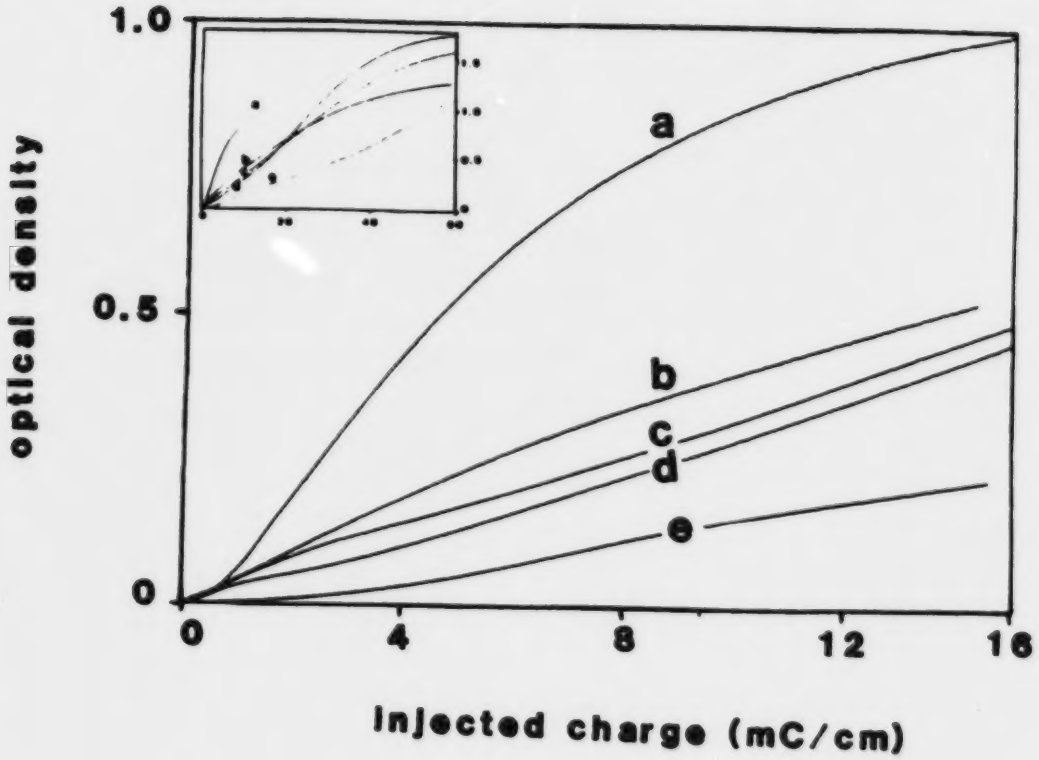


Figure 11. Variation of optical density versus injected charge

$LiClO_4$/propylene carbonate solution. Figures 9 and 10 show the cyclic voltammetry at different scanning rate for WO_3 films on ITO obtained by D.C and pulsed electrodeposition, respectively. The variation of optical density with injected charge is presented in Figure 11. Similar results were obtained for evaporated and sputtered films.

Figures 12 and 13 display the absorption spectra of WO_3 films on ITO at different applied voltages, respectively in **PAMPS** and propylene carbonate. The electrochromic properties of electrodeposited WO_3 are similar or superior than those obtained by evaporation or sputtering. Tungsten trioxide structure is confirmed by X-ray diffraction (Figure 14).

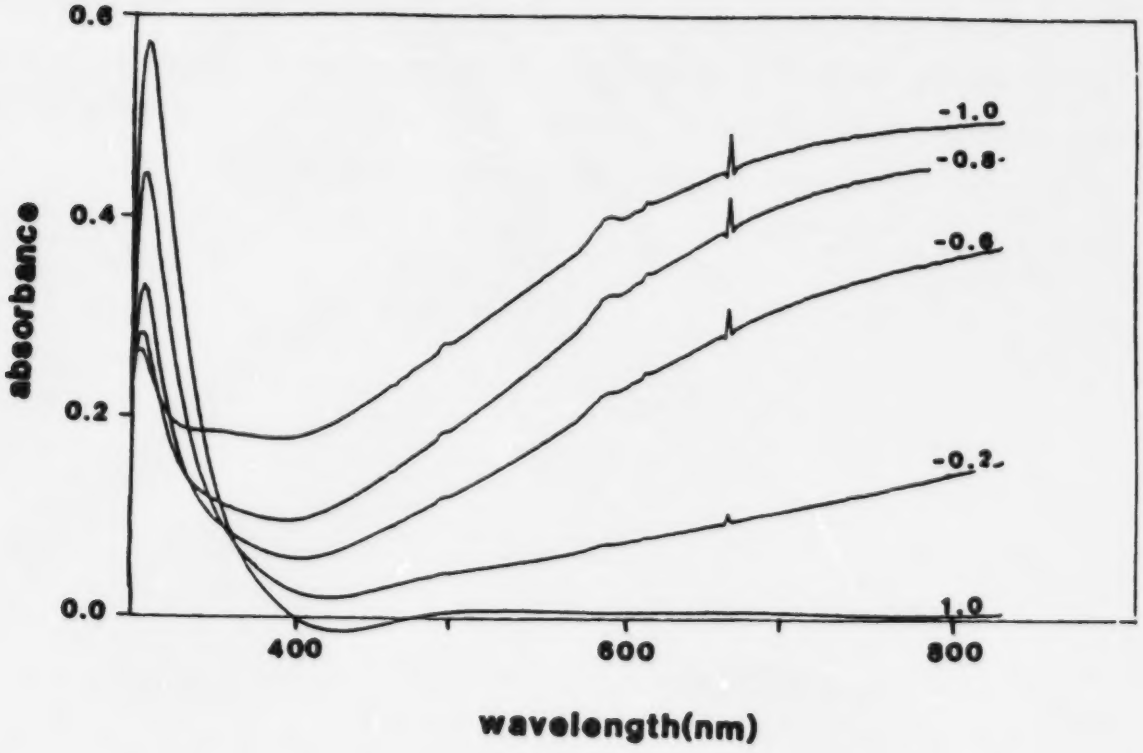


Figure 12. Spectroelectrochemistry of tungsten oxide film in PAMPS

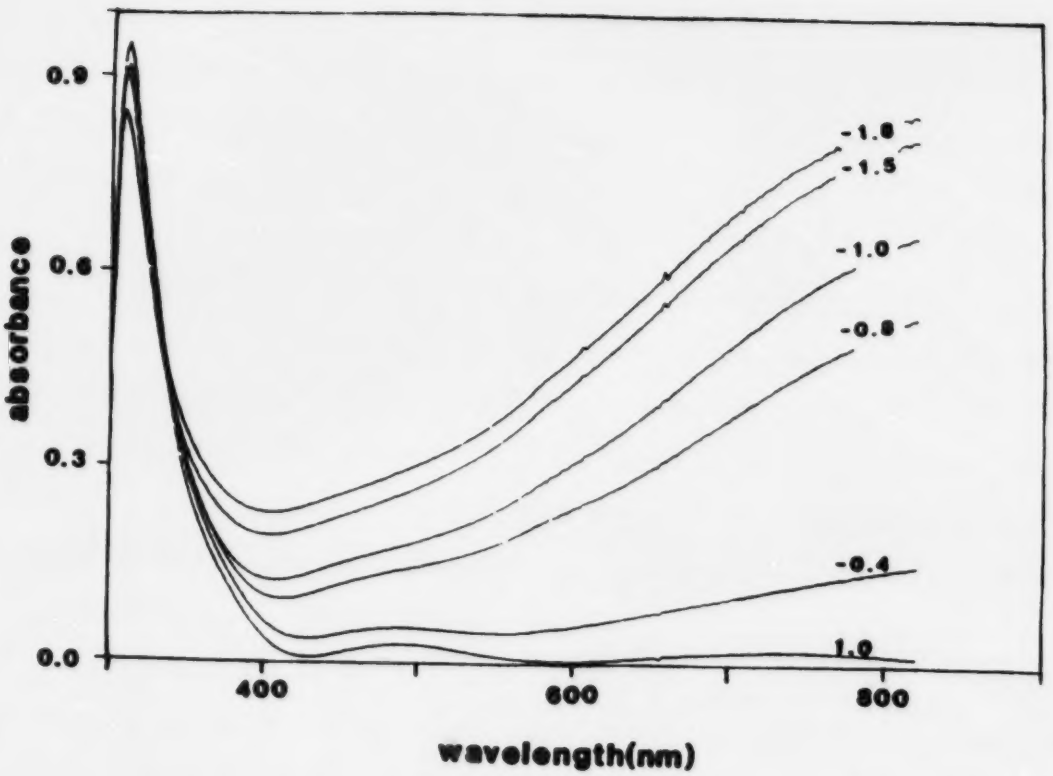


Figure 13. Spectroelectrochemistry of tungsten oxide film in propylene carbonate.

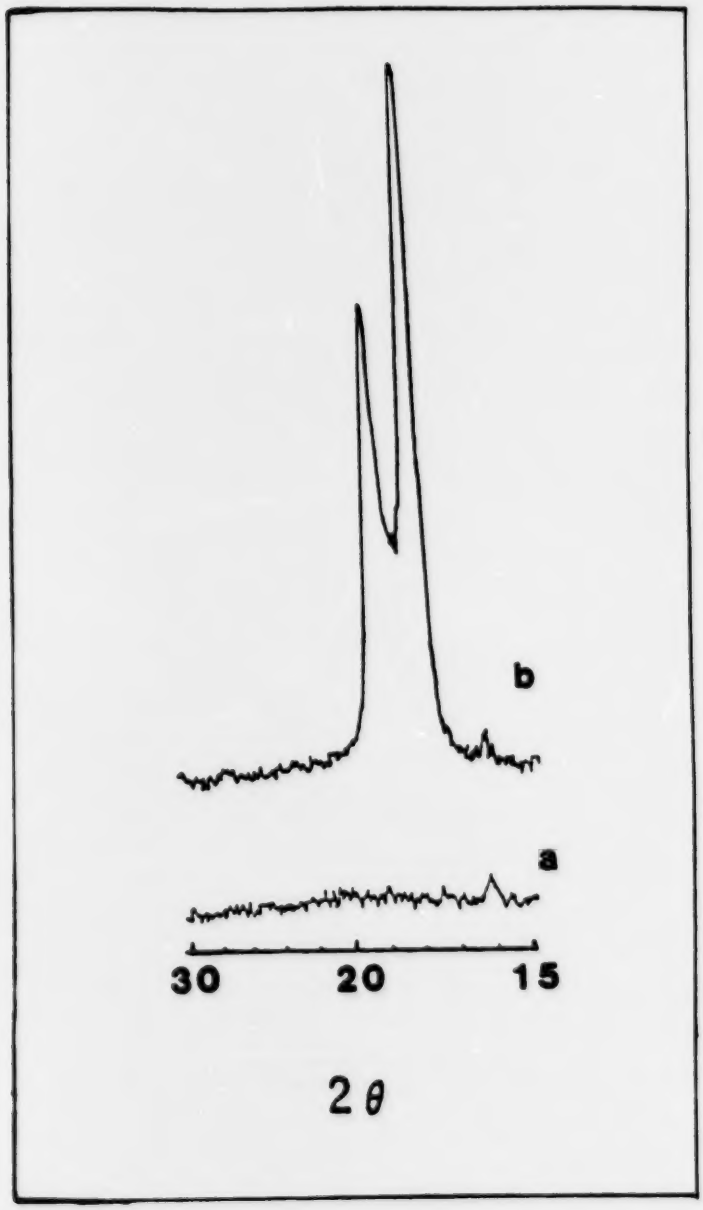


Figure 14. X-ray diffractogram of tungsten oxide film.

4.2.2. Molybdenum Oxide

Molybdenum trioxide thin films on ITO were also prepared by a propriety electrodeposition technique. Deep blue, uniform thin films of MoO_3 on ITO glass were obtained after 3 to 5 minutes by applying a fixed potential (- 10 mV) or by cycling the potential between 0 mV and - 20 mV (scanning rate of 50 mV/sec). Applied potentials more negative than - 200 mV produced electrochemically inactive brown films. Thicker films were obtained with longer deposition time, but cracks appeared when the films were dried. Contrary to WO_3 deposition, no difference was observed when a pulse voltage was used for the deposition.

Cyclic voltammograms in 1 M $LiClO_4$/propylene carbonate (PC) at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s and 4. 20 mV/s) between - 0.5 V and 2.5 V vs Ag/AgCl for an as-synthesized MoO_3 film and a heat-treated film (130 ^{0}C, 1 hr), are shown in Figures 15 and 16, respectively. As noticed before for WO_3, only well-resolved anodic peaks are observed. Heat-treated films sharpen the oxidation peak shape but have no effect on the reduction peak shape.

In correlation with the redox process, MoO_3 films exhibit multiple and reversible color changes from lightly colored to dark blue between - 0.5 V to 2.5 V. The heat-treatment also affected the reversibility and the electrochromic properties of molybdenum oxide films as shown in Figure 17. When heated to 130 ^{0}C, the film switched from light blue at 2.5 V to deep blue at - 0.4 V. The film was nearly colorless at 2.5 V when heated to 250 ^{0}C, and a good coloration-bleaching contrast could already be obtained between - 0.1 V and - 0.5 V . MoO_3 films still showed reversible redox and electrochromic behavior when heated up to 350 ^{0}C, but lost all activity at 450 ^{0}C.

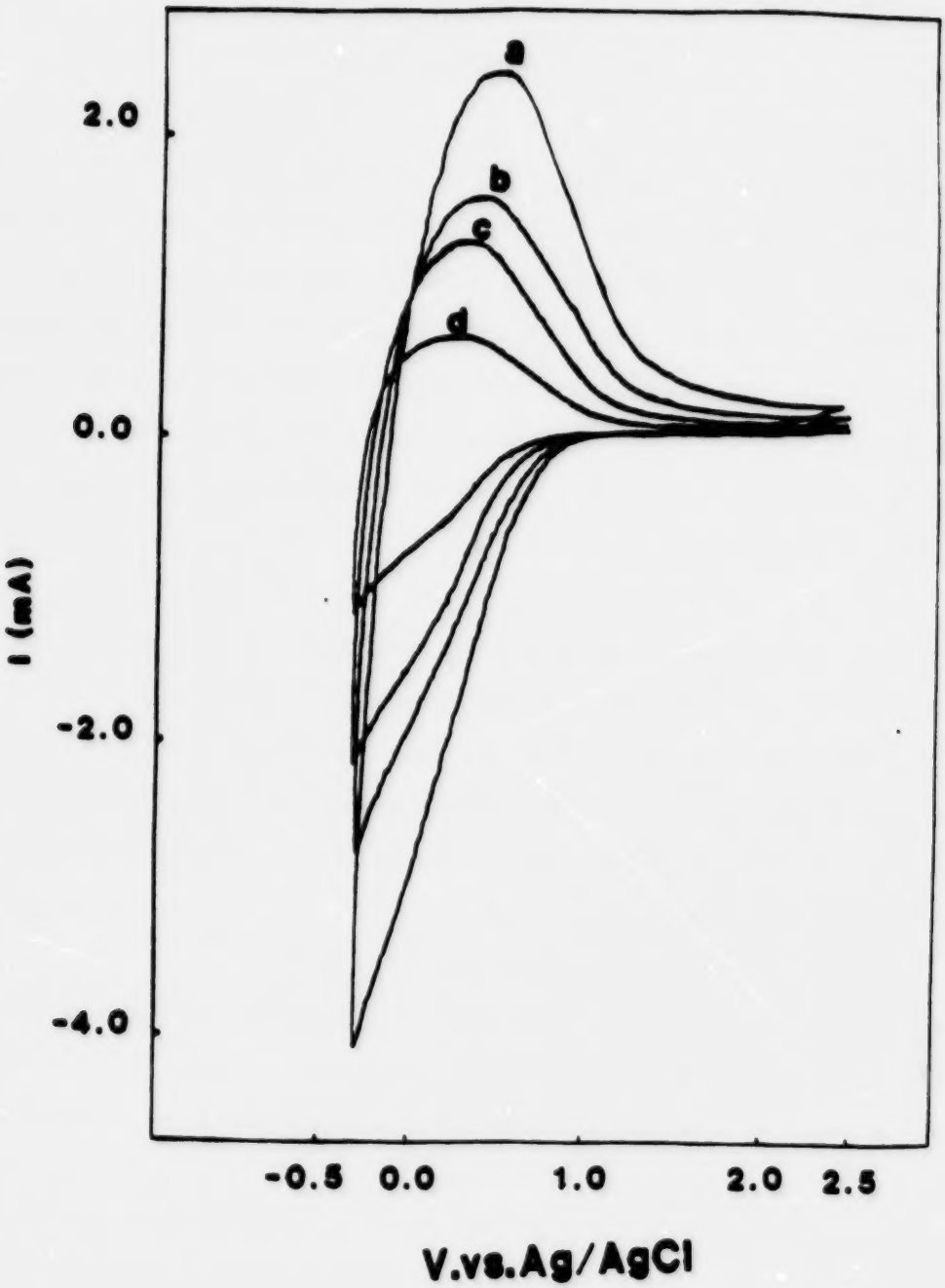


Figure 15. Cyclic voltammograms of molybdenum oxide film on ITO glass.

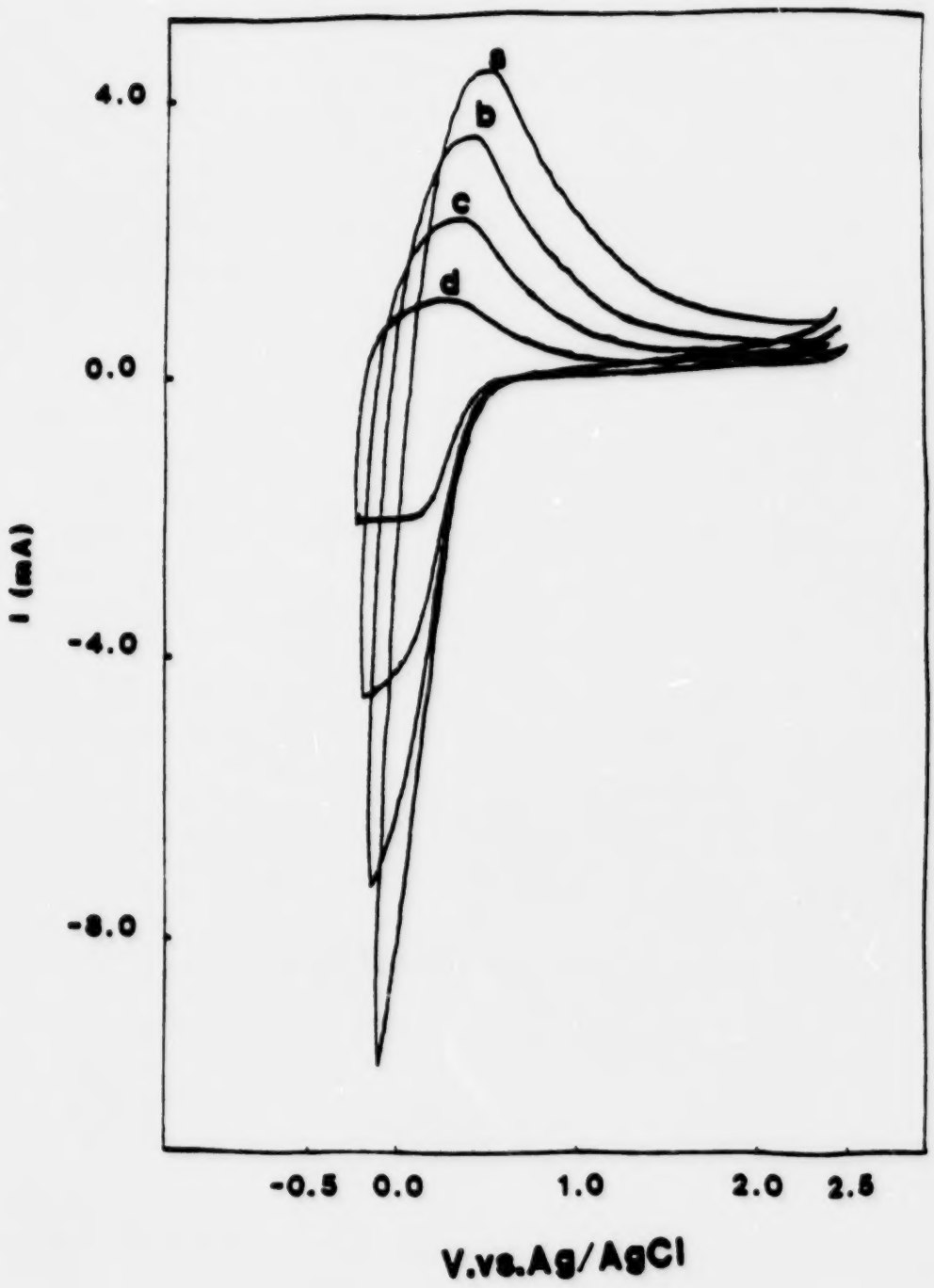


Figure 16. Cyclic voltammograms of molybdenum oxide film heated to 150 °C.

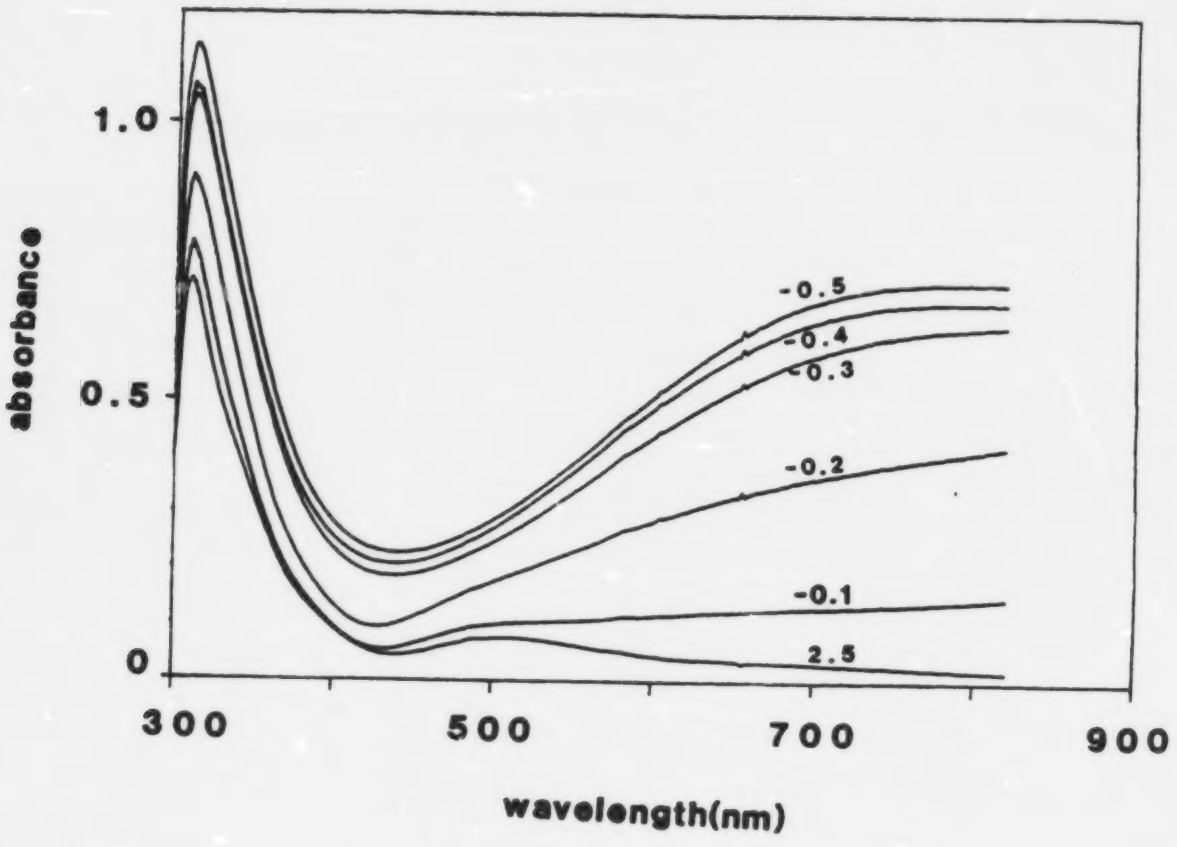


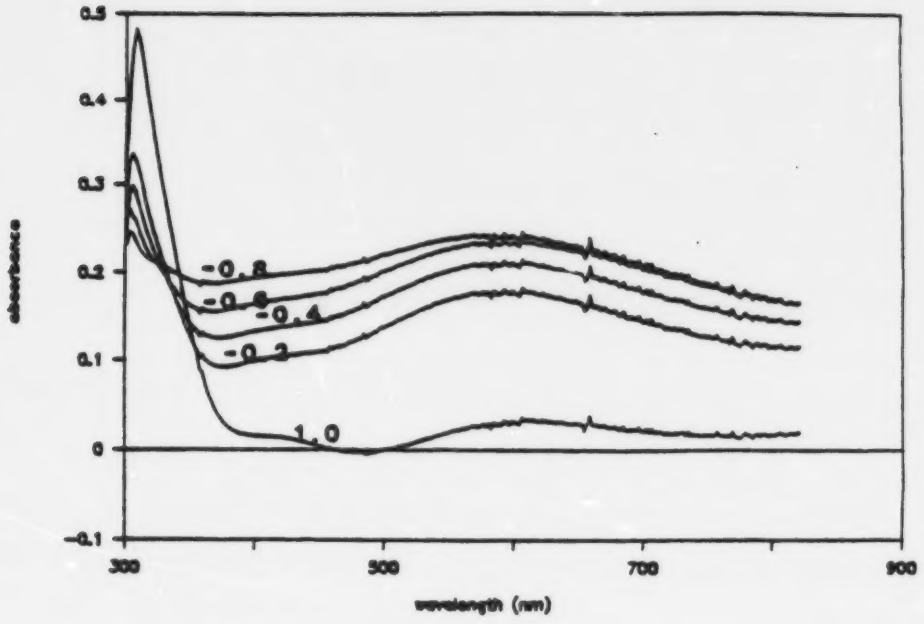
Figure 17. Spectroelectrochemistry of molybdenum oxide film on ITO in propylene carbonate.

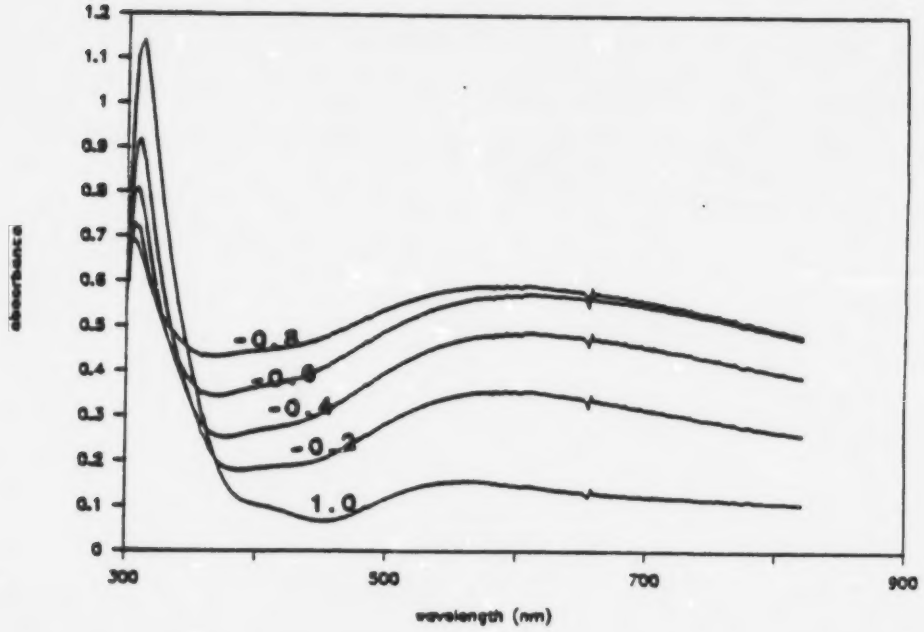
4.2.3. Doping effects

The optical and electrochemical properties of WO_3 thin films can be modulated by doping during the film preparation by different ions such as Co, Cr, Fe, Cu, Mo etc. These spectral modulation are shown in Figures 18-25.

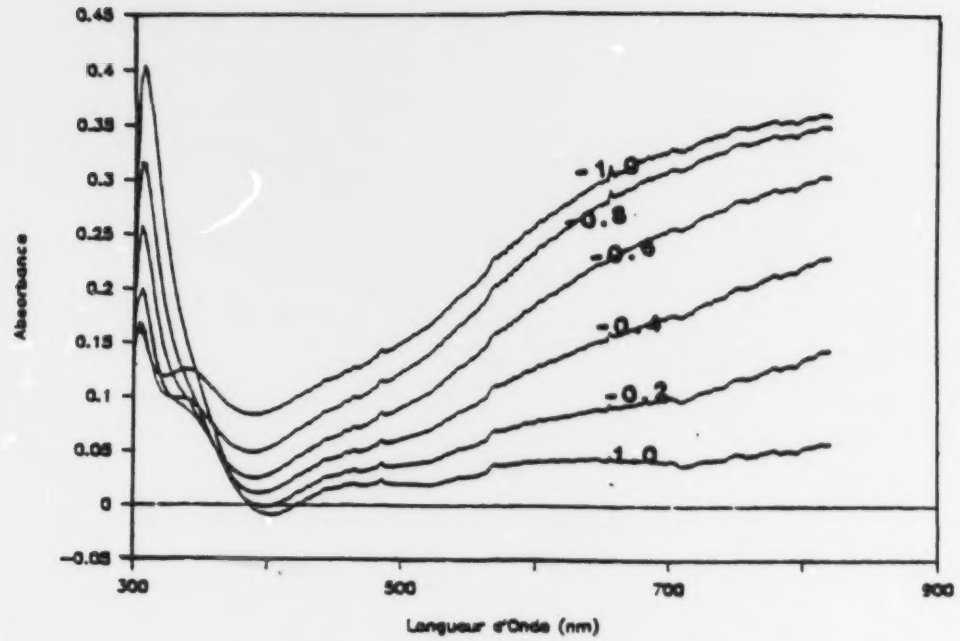
4.2.4. Conclusion

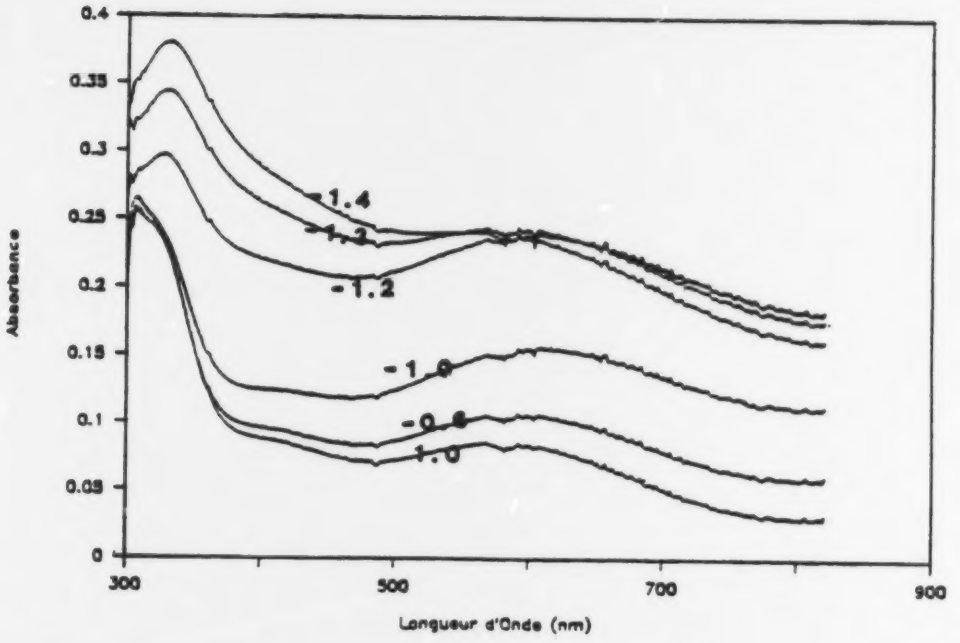
We have developed a new and simple technique to prepare transition-metal oxides thin films on transparent electrical conductors (e.g. ITO, Nesa). After a heat treatment, these materials display similar electrochemical and optical properties than those obtained by other techniques such as evaporation, sputtering or chemical vapour deposition. The electrodeposition technique used is simple and economical. Large surface can be easily prepared. Doping the transition-metal oxides with selected metals permit the modulation of their optical properties.



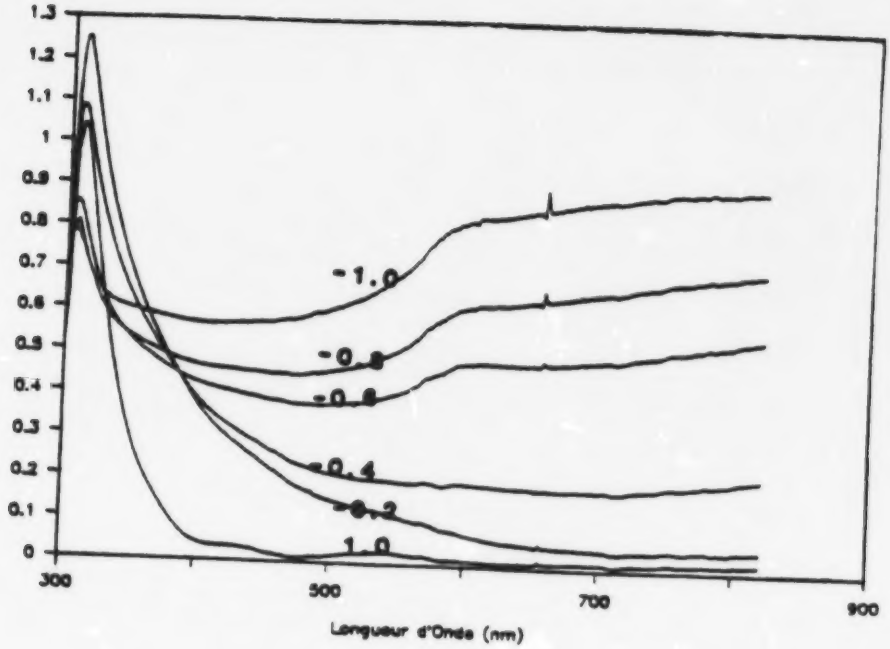


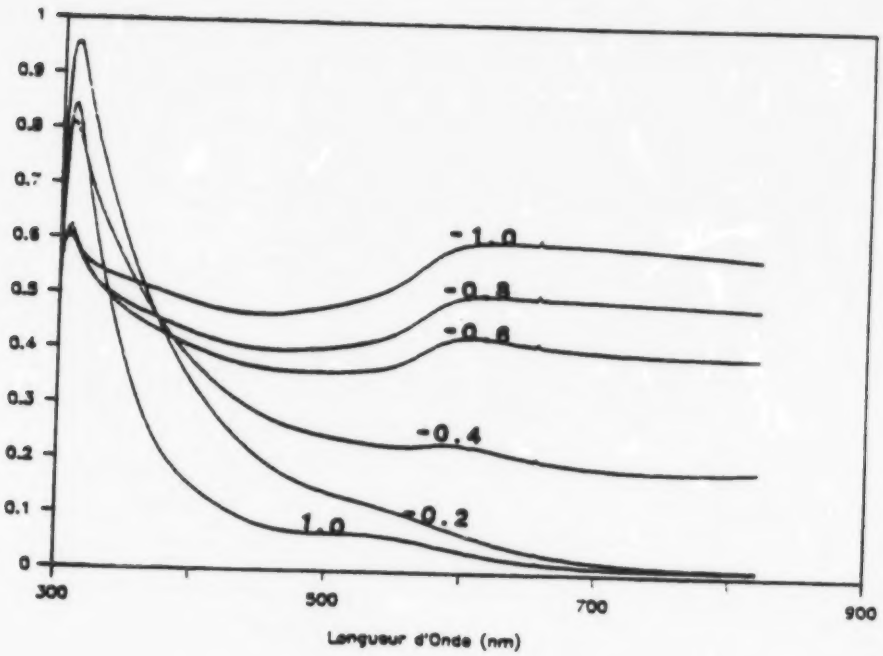
Figures 18 and 19. Tungsten oxide films doped with molybdenum.



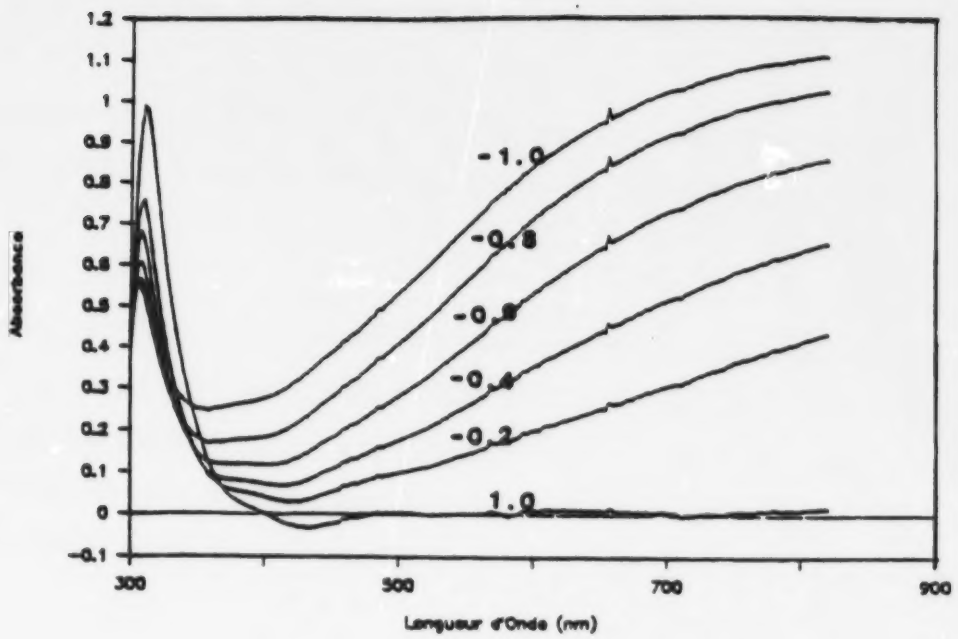


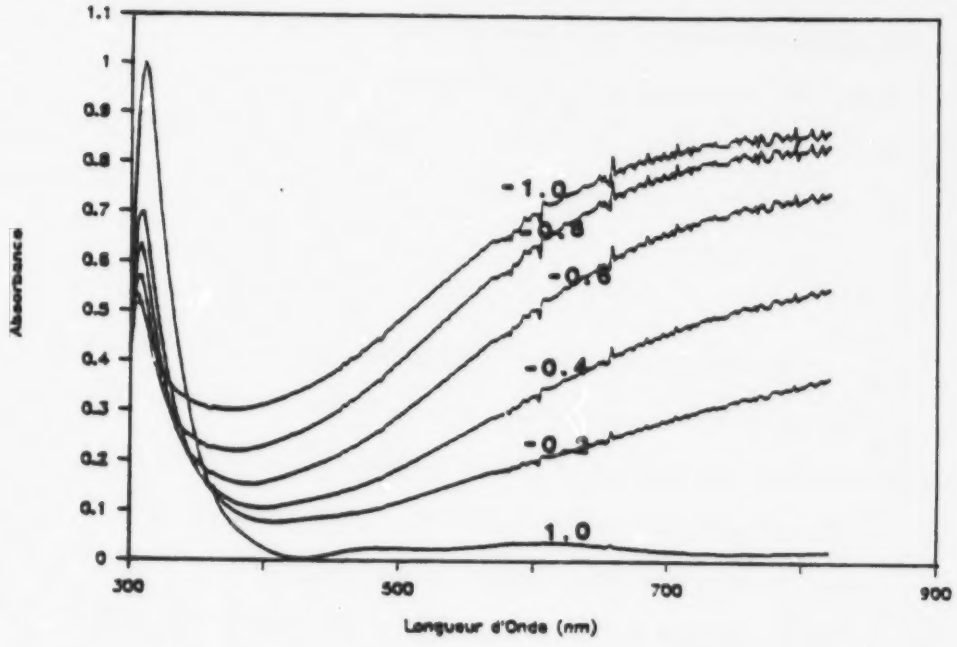
Figures 20 and 21. Tungsten oxide films doped with Co and Cr.





Figures 22 and 23. Tungsten oxide films doped with Cu.





Figures 24 and 25. Tungsten oxide films doped with Fe.

4.3. IONICALLY CONDUCTIVE ELECTROLYTE IC LAYER.

Solid polymer electrolytes were prepared and used as **IC** layer. The electrolytes were separated into two families: 1) proton (H^+) conductor electrolyte; and 2) ion (e.g. Li^+) conductor electrolyte.

For proton conductor electrolytes, we have investigated solid films of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) **PAMPS** (purchased from Aldrich Co.) and glassy films of poly(vinylalcohol)-phosphoric acid prepared in our laboratory. Usually, these polymer electrolytes gave very fast switching time, however, they also tended to degraded the electrochromic layers **EC** and the transparent electrical conductors **TEC**.

Of the number of identified candidate materials for ion conductor polymer electrolytes, we have specially investigated glassy films polyethylene oxide **PEO** gelled with propylene carbonate, polysiloxane, polyphosphazene and poly(ethyleneimine) **PEI** containing 1 M of $LiClO_4$. Most of them gave optically clear glassy films with relatively good electrical conductivities at room temperature, ranging from 10^{-3} to 10^{-6} $(ohm.cm)^{-1}$ for thin films (5 to 10 microns).

Solid, gel and glassy polymers were used as electrolytes (ion conductor). The two electrochromic layers (electron conductor) on transparent conductive glass substrates are laminated together with a layer of proton conductor (usually an acid, e.g. poly(2-acrylamido-2-methylpropanesulfonic acid) **PAMPS** or poly(vinylalcohol-phosphoric acid) **PVAP** or a layer of ion conductor, usually a salt e.g. $LiClO_4$ or CF_3SO_3Li salt in poly(ethylene) oxide-propylene carbonate **PEO** gel, poly(ethylene)imine **PEI** or photocross-linked methoxy poly(ethylene glycol methacrylate)-poly(ethylene glycol diacrylate) **MPEGM-PEGD**. The overall window structure is shown in Figure 1.

SMART WINDOW PROTOTYPES

5.1. THIN FILM DEPOSITION TECHNIQUE DEVELOPED AT INRS-ENERGIE. APPLICATIONS FOR SMART WINDOWS

Electrodeposition is a relatively common technique for the preparation of thin films of metals, semiconductors, polymers on electrical conductive materials. The technique consists of anodically or cathodically deposit the interested materials on a conductive support dipped in an electrochemical bath. Different types of control can be made: 1) d.c. deposition with current or voltage control; 2) pulsed plating with current or voltage pulses and different duty cycles. The coating is then washed, air dried or fired in an oven to densify the newly formed coating.

Successful electrodeposition requires that:

a. The solution must have an adequate shelf life. It must not decompose within the expected usage lifetime.
b. The solution must coat the substrate evenly. The film obtained must have the same thickness and the same density (reproducibility).
c. The applied voltage must be relatively low (maximum +/- 2 V).
d. The coating must be functional. It must have the desired hardness, adhesion, electrical, optical property, etc.

Advantages of the electrodeposition technique include:

a. For transition-metal oxides, the coating compare favourably to vacuum techniques such as electron-bean evaporation, reactive sputter deposition (d.c. or r.f.) or chemical vapour deposition.

b. Electrodeposition is a non-vacuum technique. Therefore, equipment is relatively inexpensive.

c. The process can be scaled and amenabled to coat very large surface.

e. The thickness of coating is easily controlled by a coulometer or an amperometer. Good uniformity over a large surface can be obtained.

d. The doping can be directly introduced during the electrodeposition. Deposition of mixed oxide is relatively easy.

e. Both sides of the electrical conductive glass can be coated simultaneously.

Problems still exist. The quality of the coating depends on the quality of the electrically conductive glass. Electrical contacts are often the main problem for a good deposition. Electrolytes and monomers often remain in the coating. Extensive washing and drying are often necessary.

Overall, the electrodeposition technique is a very suitable technique for economical deposition of large surface.

We have developed the electrodeposition technique for coating large flat surface glasses with a variety of electrochromically active materials. This technique was used to prepare anodically and cathodically electrochromic layers of a five-layer structural "smart" window device. Coating deposited to date include:

a. Anodic materials

- Poly(aniline)
- Poly(alkylanilines)
- Poly(N-alkylanilines) e.g. poly(N-benzylaniline)
- Poly(arylanilines)
- Poly(N-arylanilines) or poly(diarylamines), e.g. poly(diphenylamine)

b. Cathodic materials

- Tungsten oxide
- Molybdenum oxide
- Vanadium oxide
- Nickel oxide
- Mixtures

Generally, the electrochemical cell used for the electrodeposition is a rectangular fish tank in plastic for aqueous solution and in glass for organic solvents. The design is relatively simple, the glass electrode is placed parallel to a metallic electrode (nickel or aluminum foils) in an electrolytic bath . Electrical contacts are made with copper wires which are connected to a potentiostat for potential control or a power source for current control. For very large flat glass, a dip coater is necessary (Figure 26). The transparent glass electrode is withdraw from the electrolytic bath by the dip coater during the electrodeposition. Relatively uniform coatings of electrochromic films on 35 by 35 cm ITO glass were obtained.

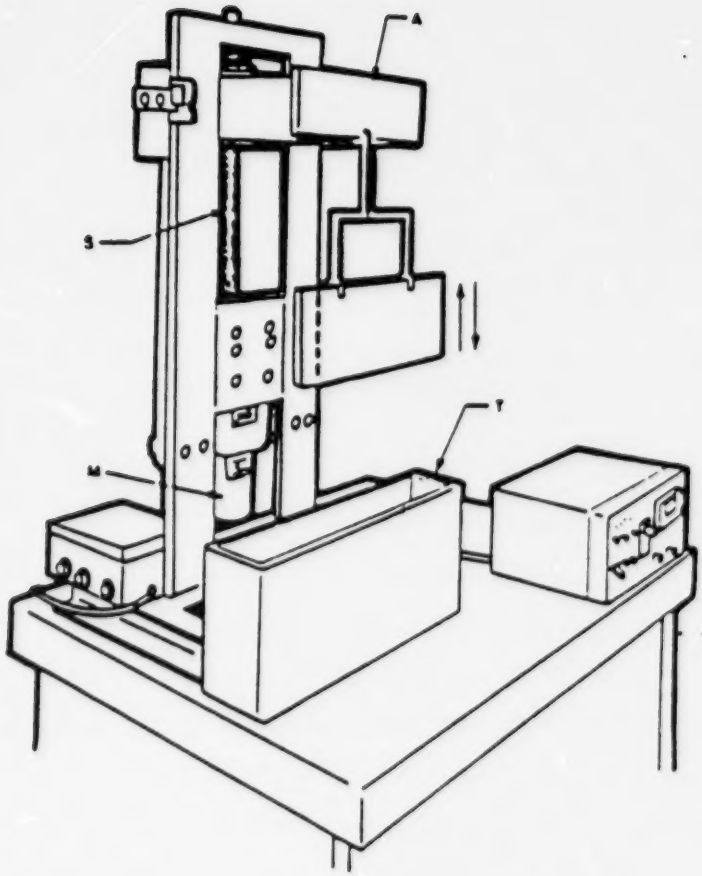


Figure 26. Dip coater.

5.2. PROTOTYPES DEVELOPED AT INRS-ENERGIE

We have successfully prepared protype three-layer, four-layer and five-layer smart window devices. Five-layer devices which are in fact an electro-optically active battery, are probably the most useful for relatively large area applications such as windows. Different devices were fabricated and studied:

SnO_2/Poly(BAn)/PAMPS/WO_3/SnO_2	**Prototype I**
ITO/Poly(DPA)/PEO/WO_3/ITO	**Prototype II**
ITO/Poly(DPA)/PEI/WO_3-MO_3/ITO	**Prototype III**
ITO/Poly(DPA)/MPEGM-PEGD/WO_3/ITO	**Prototype IV**

where poly(N-benzylaniline), **Poly(BAn)**, and poly(diphenylamine) **Poly(DPA)** are the electrochromic layers **EC** and **WO_3** or **WO_3-MO_3** are the electrochromic counter-electrode layers **CE**; all of them were prepared by electrodeposition. A proton conducting polymer electrolyte (**Poly(AMPS)**) layer **IC** was used for prototype I and ion conductor polymer electrolytes (**PEO, PEI, MPEGM-PEGD**) were used for prototypes II, III and IV.

Additional information about these prototypes can be found in the reprints 6, 7 and 8 in the appendix.

5.2.1. Prototype I: SnO_2/Poly(BAn)/Poly(AMPS)/WO_3/SnO_2

We report here a new solid-state electrochromic prototype:

SnO_2/Poly(BAn)/Poly(AMPS)/WO_3/SnO_2

where poly(N-benzylaniline), **Poly(BAn)**, and **WO_3** are the electrochromic thin films prepared by electrodeposition and poly(2-acrylamido-2-methylpropanesulfonic acid), **Poly(AMPS)**, the proton conducting polymer electrolyte film.

WO_3 thin films (1-3 μm) were obtained from tungsten-hydrogen peroxide solution on tin-oxide glass (30 ohm/square, 10 x 10 cm^2) in a one-comportment cell using Ni foil and Ag/AgCl (3.8 M KCl) as counter and reference electrodes, by cycling the potential between -400 mV and -800 mV at a scanning rate of 60 mV/s. Pulsed plating electrodeposition was also successfully used and high quality films were obtained. The deep blue films were extensively rinsed with water and then thermally treated for one hour at 130°C. Uniform green poly(N-benzylaniline) films were obtained from aqueous solution of 0.1 M N-benzylaniline in 1.0 M phosphoric acid, in a similar cell, by scanning the potential between +400 mV and +800 mV vs Ag/AgCl. The two electrochromic electrodes were assembled as shown in Figure 1 with a thin layer of Poly(AMPS) (80 % in water) as electrolyte.

The cyclic voltammogram of prototype I is shown in Figure 27. For comparison, cyclic voltammograms of WO_3 and Poly(BAn) on tin-oxide in Poly(AMPS) with a Ni counter-electrode are shown in Figures 28 and 29, respectively. No well defined redox peaks were observed for the prototype I compared to its components.

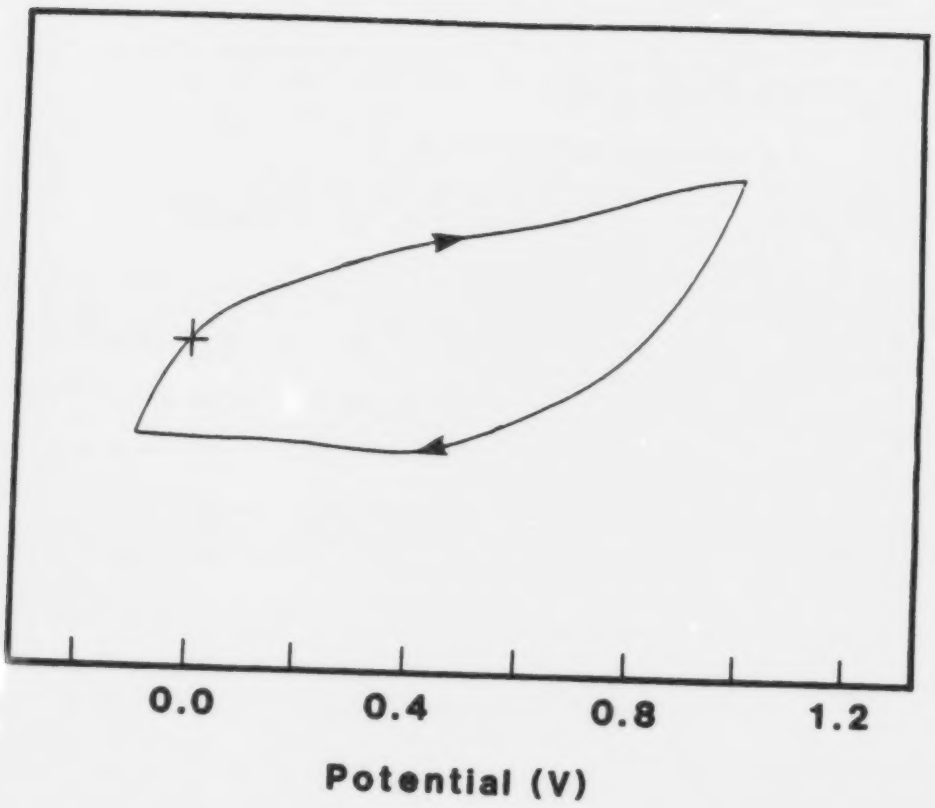


Figure 27. Cyclic voltammogram of prototype I.

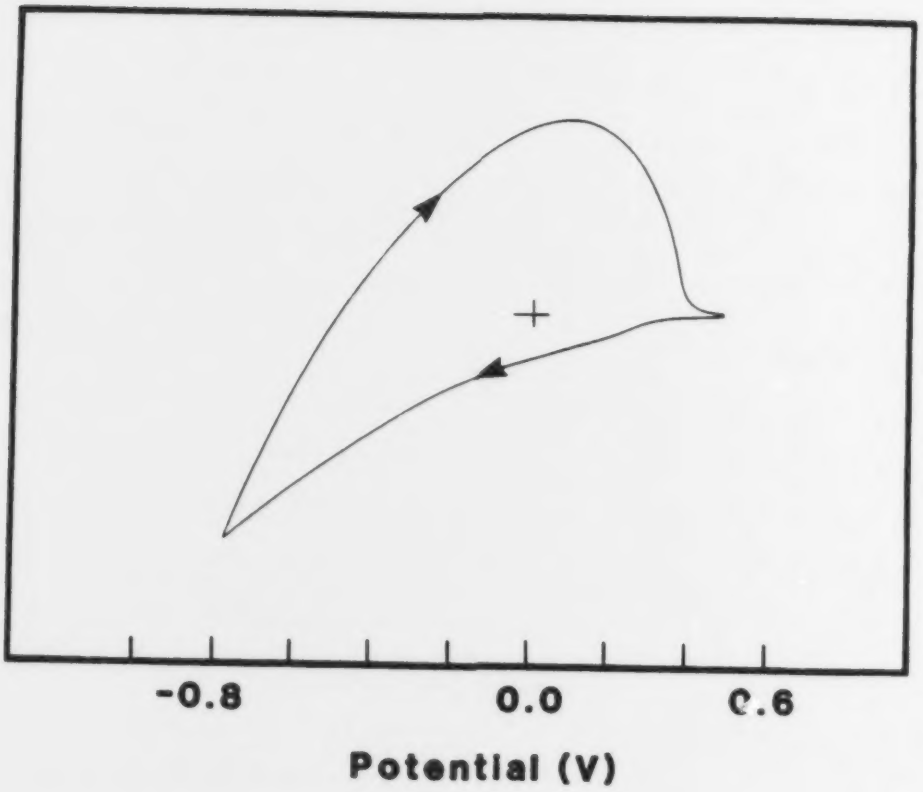


Figure 28. Cyclic voltammogram of tungsten oxide film.

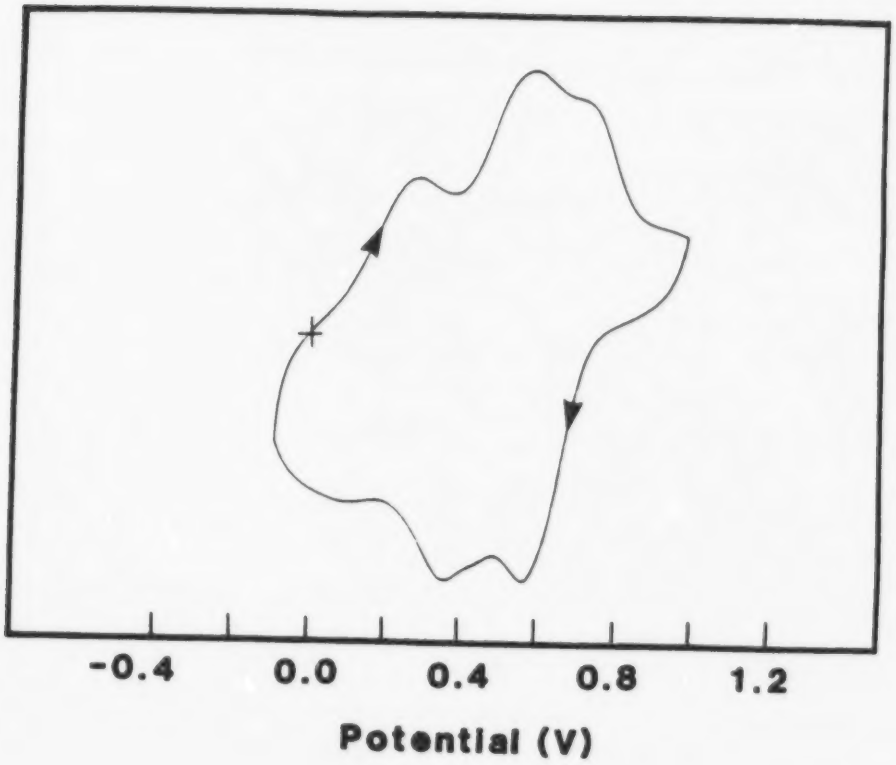


Figure 29. Cyclic voltammogram of poly(N-benzylaniline) film.

In effect, WO_3 films show the same redox shape as reported in the literature and Poly(BAn) films present two redox couples corresponding to the polaron and bipolaron formation.

As the applied voltage was varied, the colour of Poly(BAn) film reversibly changed from pale transparent yellow in the reduced state (0.0 V vs Ag/AgCl) to dark green in the oxidized state (0.8 V). The WO_3 film also reversibly changed its colour from colourless in the oxidized state (0.4 V) to dark blue in the reduced state (-0.8 V) vs Ag/AgCl. Hence, the combined colours of the prototype I, with Poly(BAn) as working electrode and WO_3 as counter-electrode, changed from transparent clear yellow at -0.1 V to deep blue at 1.0 V as shown in Figure 30.

Prototypes I were repetitively cycled more than 10^5 times between the bleached and the coloured states without apparent degradation. The devices were also left at room temperature for 16 days in the bleached state (80 % transmittance) and the coloured state (20 % transmittance). The variations of the transmittance at 700 nm for the bleached and coloured states were followed in the time (Figure 31, curves a and b). The variations in the transmittance observed after many days were mainly due to the degradation of WO_3 by the residual water in Poly(AMPS). Better long term stability was obtained with a non-aqueous solid electrolyte such as poly(ethylene oxide) PEO-$LiClO_4$ system (Figure 31, curves c and d).

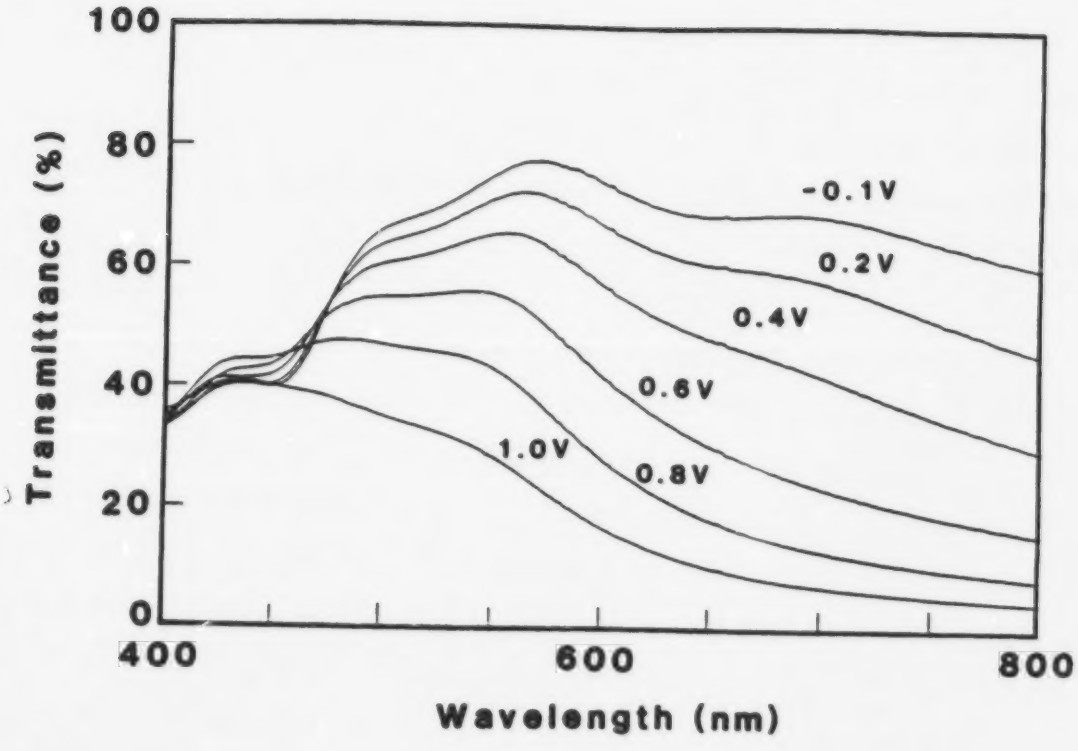


Figure 30. Spectroelectrochemistry of prototype I.

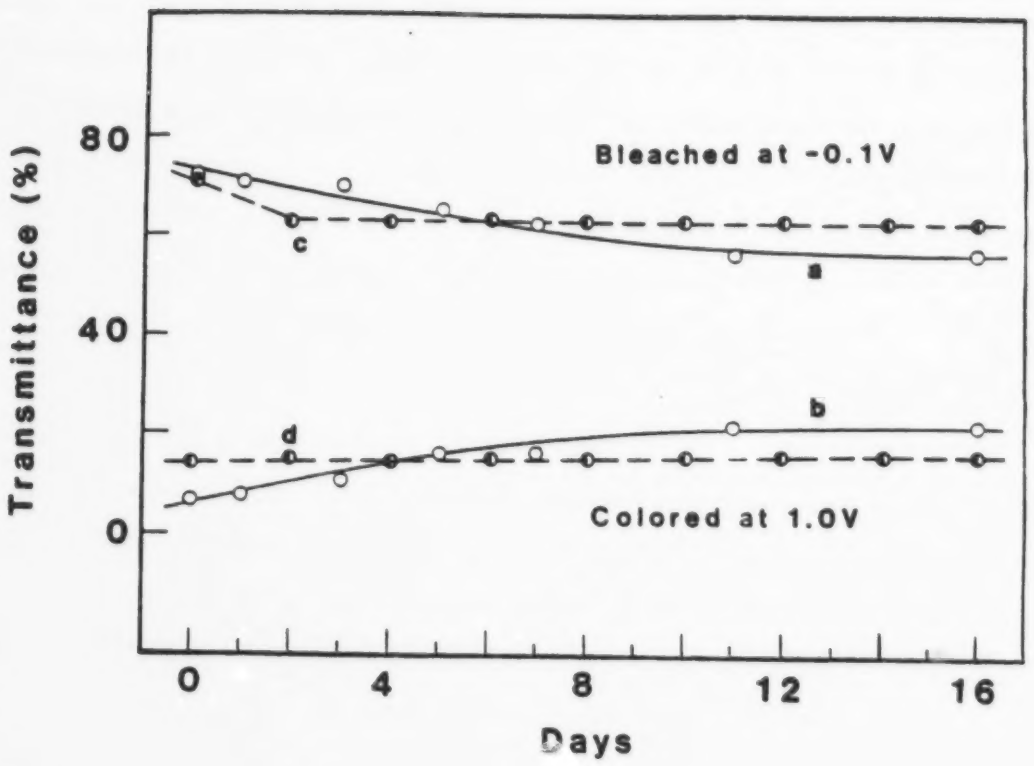


Figure 31. Stability of prototype I in PAMPS (curves a and b) and in PEO (curves c and d).

5.2.2. Prototype II: ITO/Poly(DPA)/PEO/WO_3/ITO

The cyclic voltammogram of Prototype II is shown in Figure 32. For comparison, cyclic voltammograms of WO_3 and Poly(DPA) films on ITO dipped in 1M $LiClO_4$/propylene carbonate with a Ni counter-electrode are shown in Figures 33 and 34. As observed before, only one oxidation peak is observed for WO_3 when the potentials were scanned between -0.8 and 0.6 V vs. an Ag/AgCl reference electrode (Figure 33). Poly(DPA) film presents two oxidations peaks at 0.5 and 0.85 V vs. Ag/AgCl (Figure 34). These oxidation peaks are related to the polaron and bipolaron formation. In correlation with these redox processes, WO_3 and poly(DPA) films show multiple and reversible colour changes. Visible transmittance spectra of these films dipped in 1.0 M $LiClO_4$/PC at different applied voltage are shown in Figures 35 and 36.

Prototype II, contrary to its components, presents no well defined redox peaks (Figure 32) when the applied potentials were scanned between - 0.2 and 1.2 V. However, as the applied voltages were changed, **Prototype II** exhibits multiple and reversible colour transformation from pale yellow at - 0.2 V to deep blue at 1.2 V. The transmittance spectra of **Prototype II** at different applied voltages between the bleached state (- 0.1 V) and the coloured state (+ 1.0 V) are shown in Figure 37.

The response time of **Prototype II** (60 sec) is quite acceptable for an all solid-state prototype when the applied voltage is switched between 1.5 and - 1.5 V (transmittance between 83 and 13 %) as shown in Figure 38.

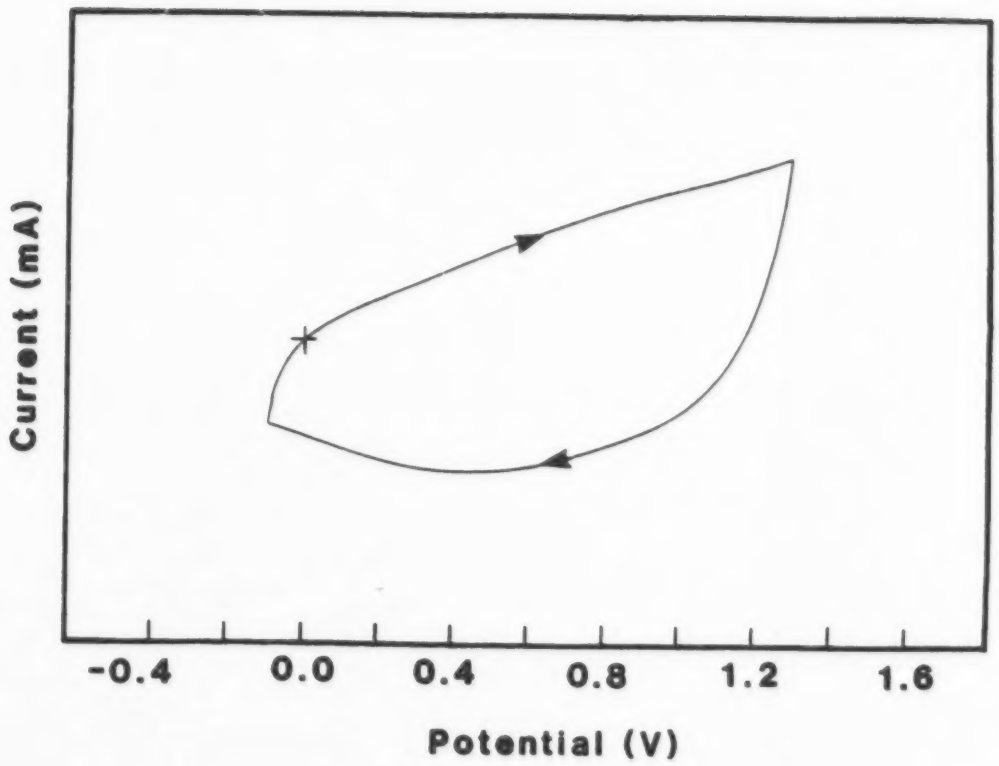


Figure 32. Cyclic voltammogram of prototype II.

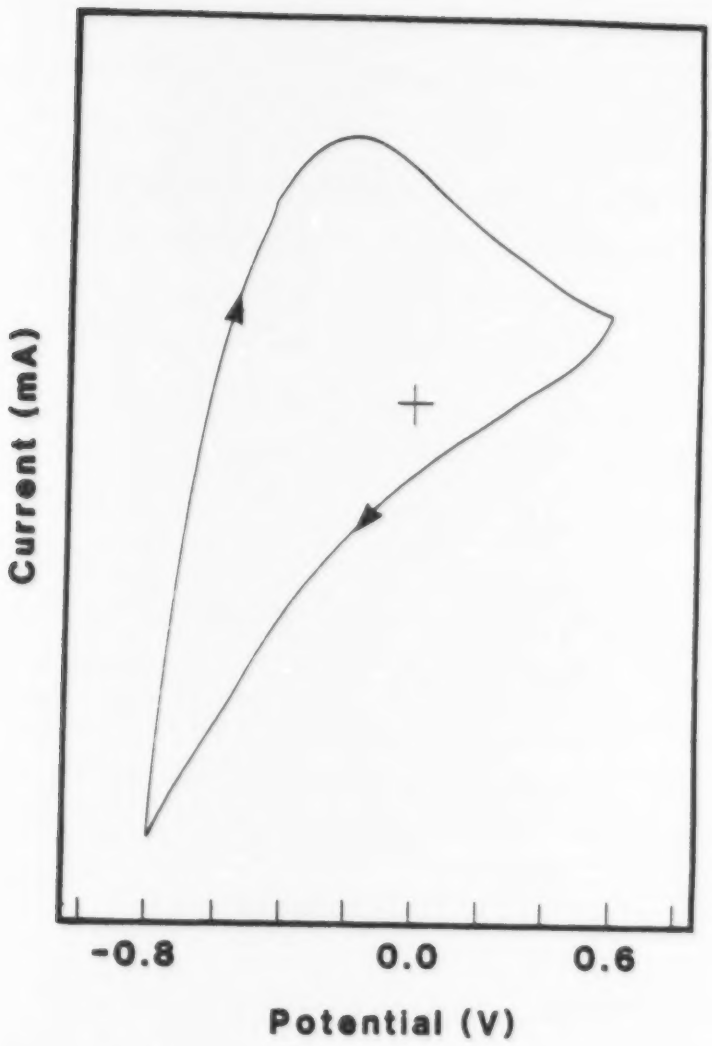


Figure 33. Cyclic voltammogram of tungsten oxide in propylene carbonate.

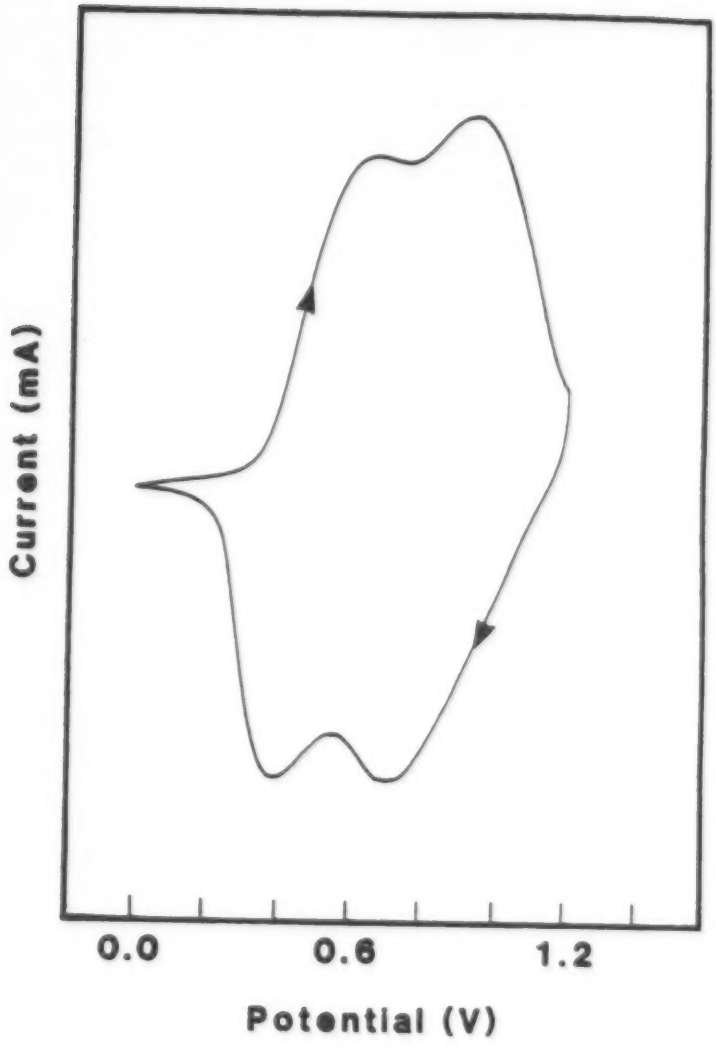


Figure 34. Cyclic voltammogram of poly(DPA) film in propylene carbonate.

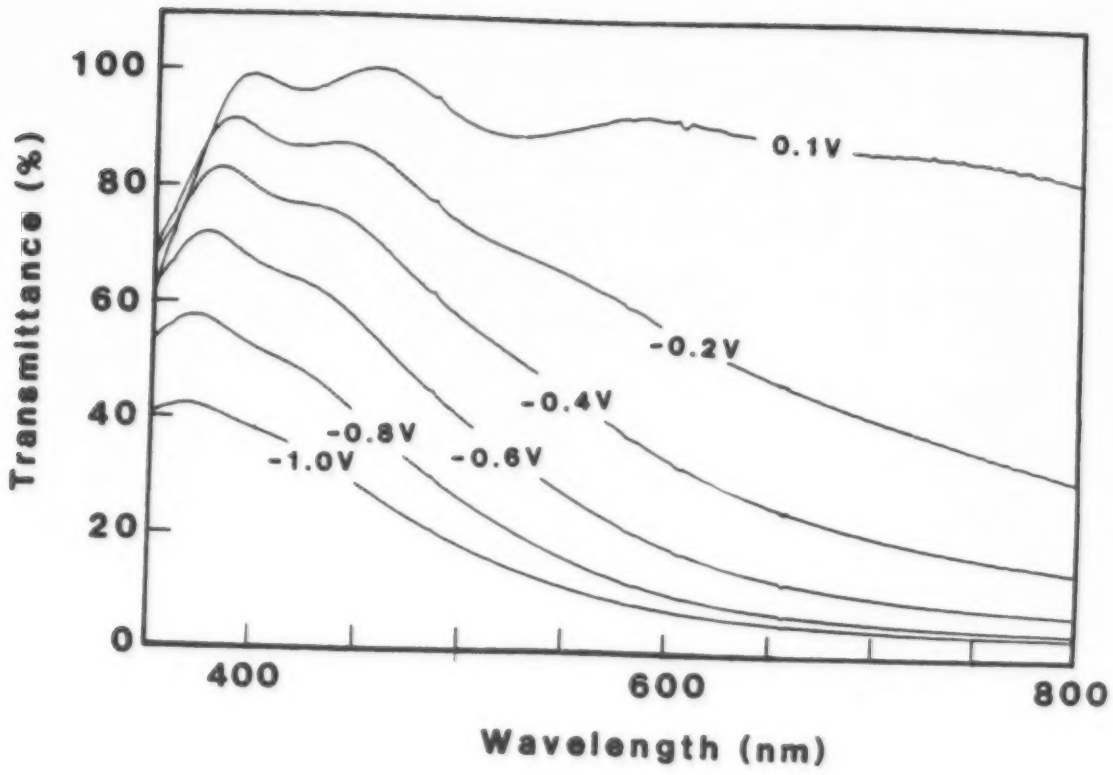


Figure 35. Transmittance spectra of tungsten oxide film at different applied potentials.

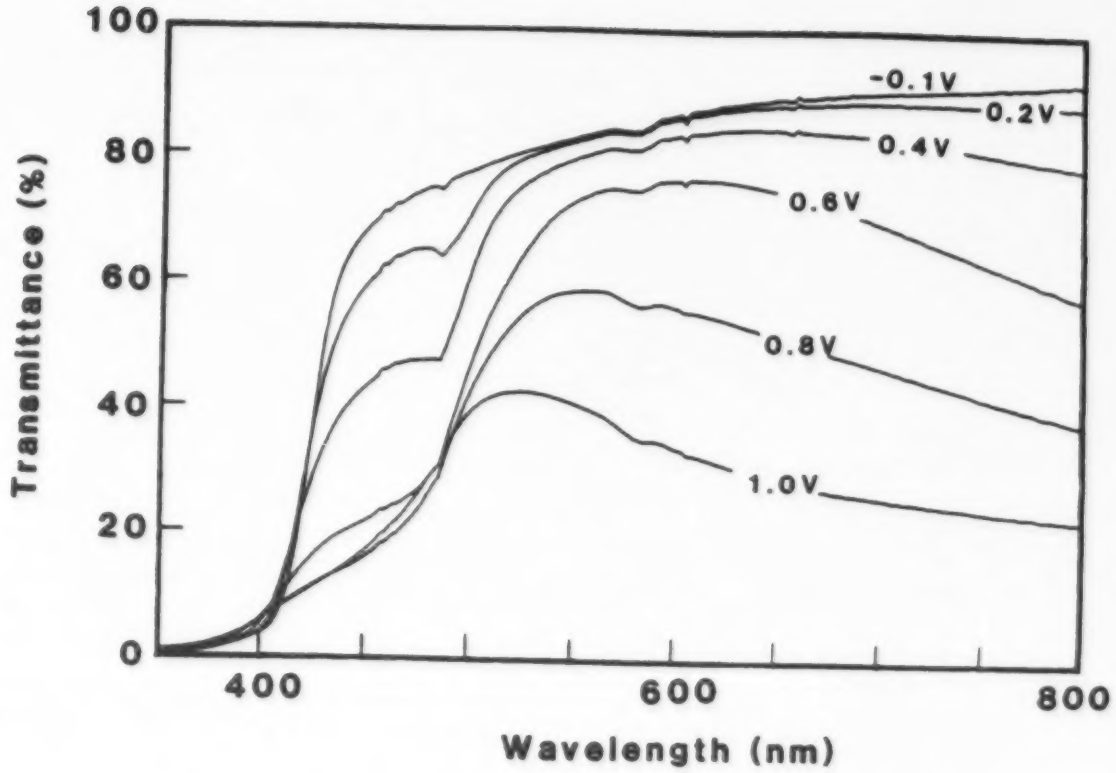


Figure 36. Transmittance spectra of poly(DPA) film at different applied potentials.

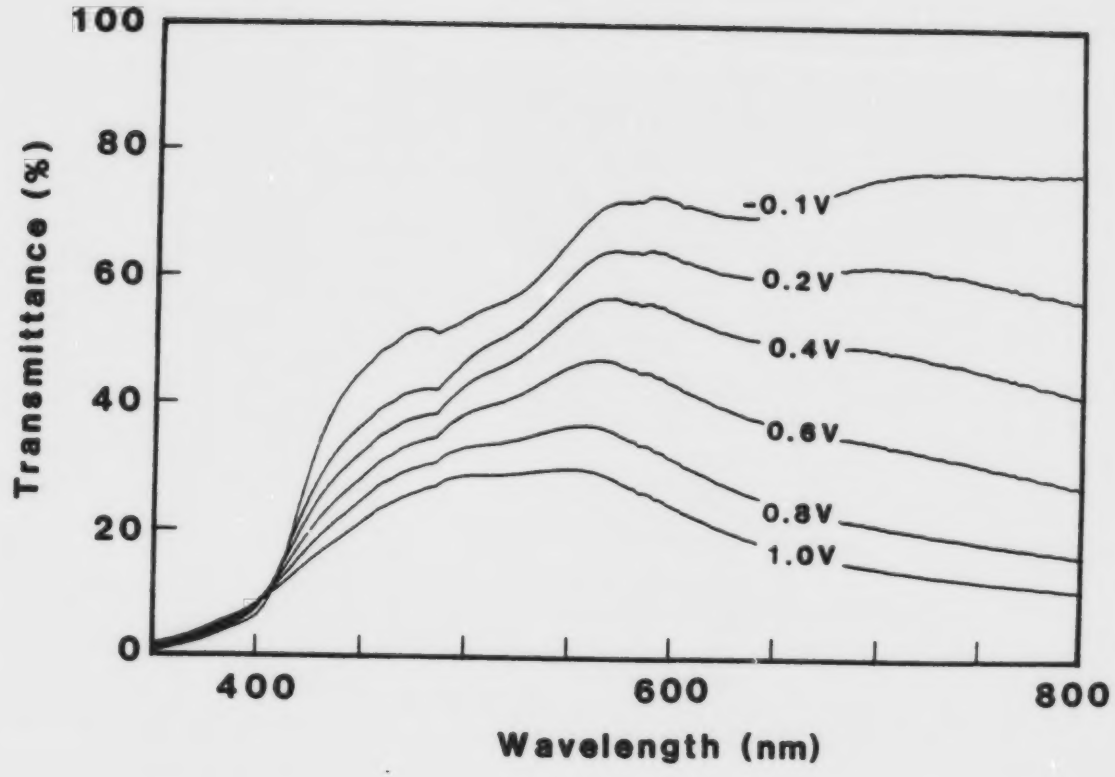


Figure 37. Spectroelectrochemistry of prototype II.

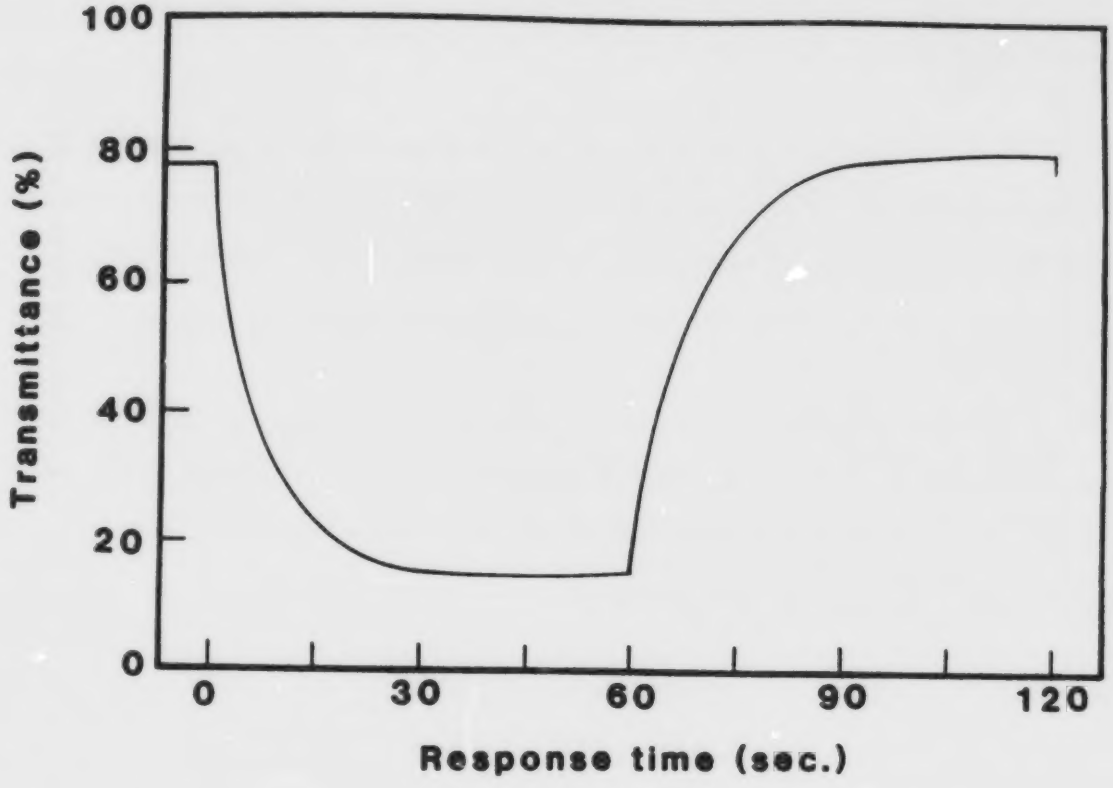


Figure 38. Switching response time of prototype II.

The prototype II was left at room temperature for 16 days in the bleached state (62 % transmissivity) and in the coloured state (16 %), and the variation in transmissivity was measured. No significant variation is noticed as can be seen in Figure 31.

Prototype II was also submitted to deep and complete charge and discharge cycles (+/- 1.5 V) and the result is shown in Figure 39. The coloured state seems to be more strongly affected than the bleached state, and after 15 thousand cycles, the contrast (coloured and bleached states) dropped more than 30%.

The self-discharge curve of Prototype II is shown in Figure 40. The Prototype II was charged at 1.0 V and the variation of the transmittance at 700 nm in the open circuit was followed in the time. The electrochromic Prototype lost about 30 % of transmittance after 24 h.

The long term stability and the coloration contrast are strongly influenced by the electrolyte used. In order to improve the characteristic and stability of the window prototype, a new electrolyte based on poly(ethylene imine) was used.

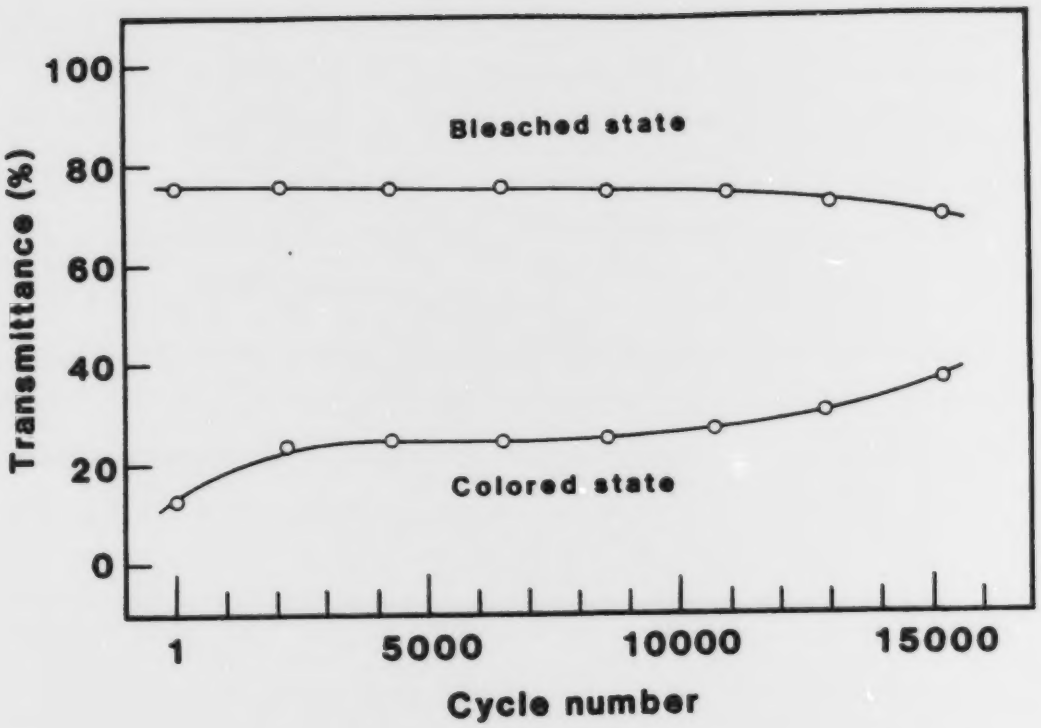


Figure 39. Stability of prototype II

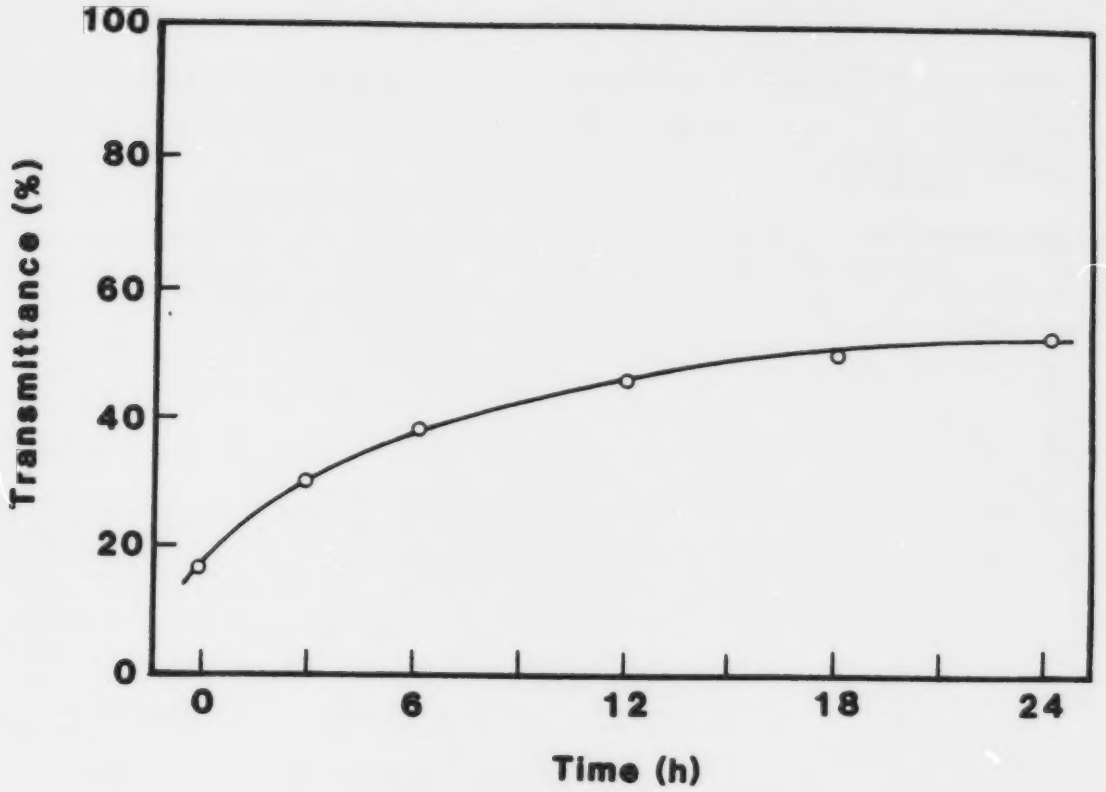


Figure 40. Open circuit memory of prototype II.

5.2.3. Prototype III: ITO/Poly(DPA)/PEI/WO_3-MO_3/ITO

The transmission spectra of Prototype III at different applied voltages are shown in Figure 41. The prototype III changed it colour from colourless at - 0.1 V (80 % transmittance) to deep dark blue at 2.0V (5 % transmittance at 800 nm).

The response times of prototype III at room temperature pass from 6 min for an applied voltage of 2.0 V (full line) to about 3 min for a higher applied voltage (2.5 V) (broken line) as shown in Figure 42. Although its switching time is slightly slower than prototype II, prototype III has better kept its charge as shown in Figure 43.

The open circuit voltage decay of prototype III charged at 2.0 V shows a far better self-discharge (about 20 % of transmittance variation) after 5 days compared to prototype II. In fact, prototype III is very stable and no significant change in its properties has been observed after 6 months of cycling testing.

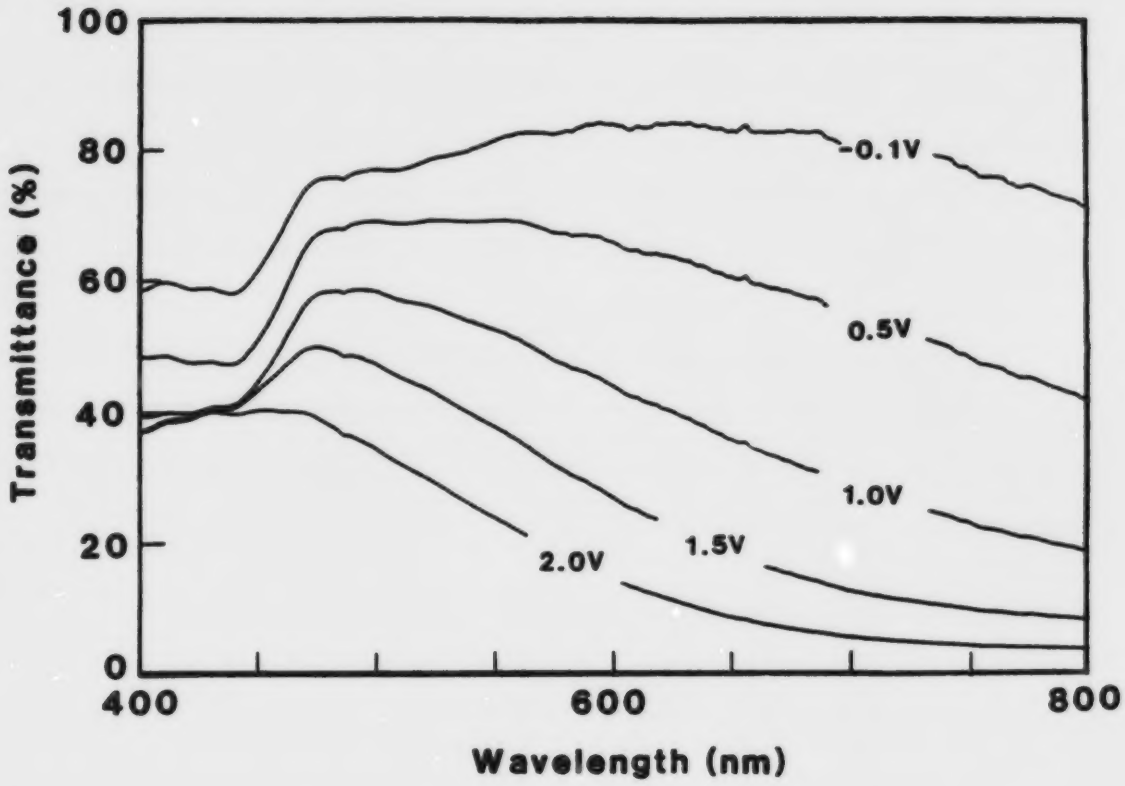


Figure 41. Transmittance of prototype III at different applied potentials.

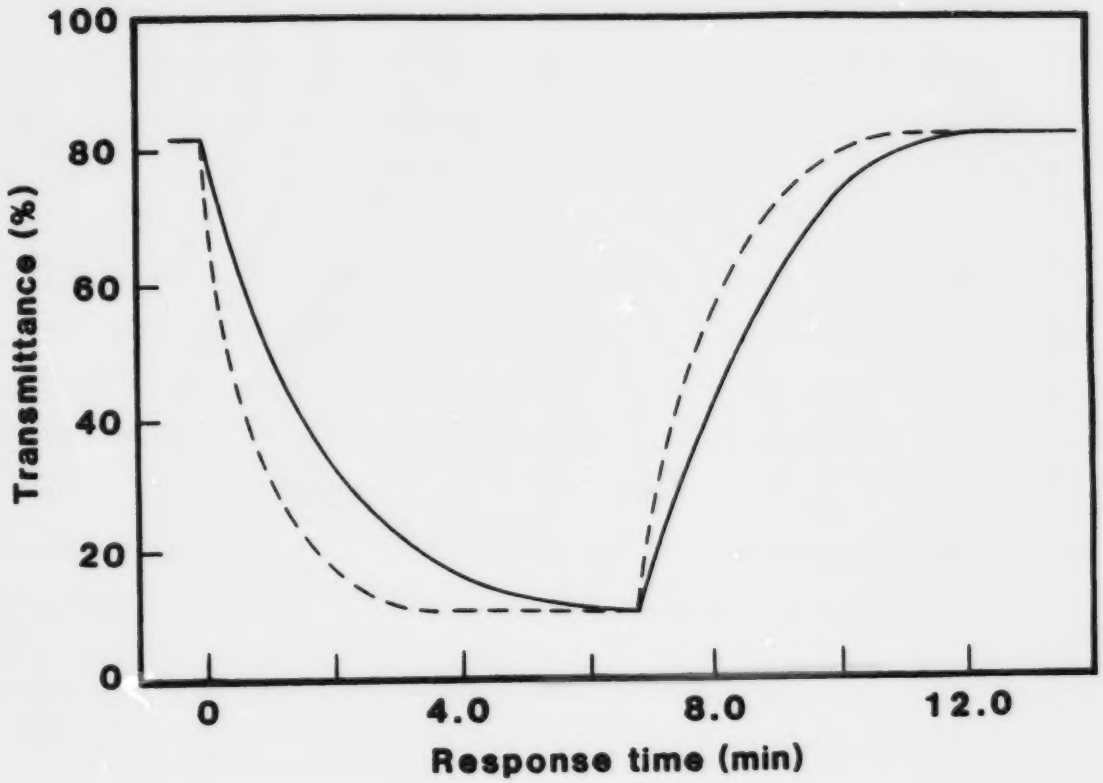


Figure 42. Switching response time of prototype III at different applied voltages.

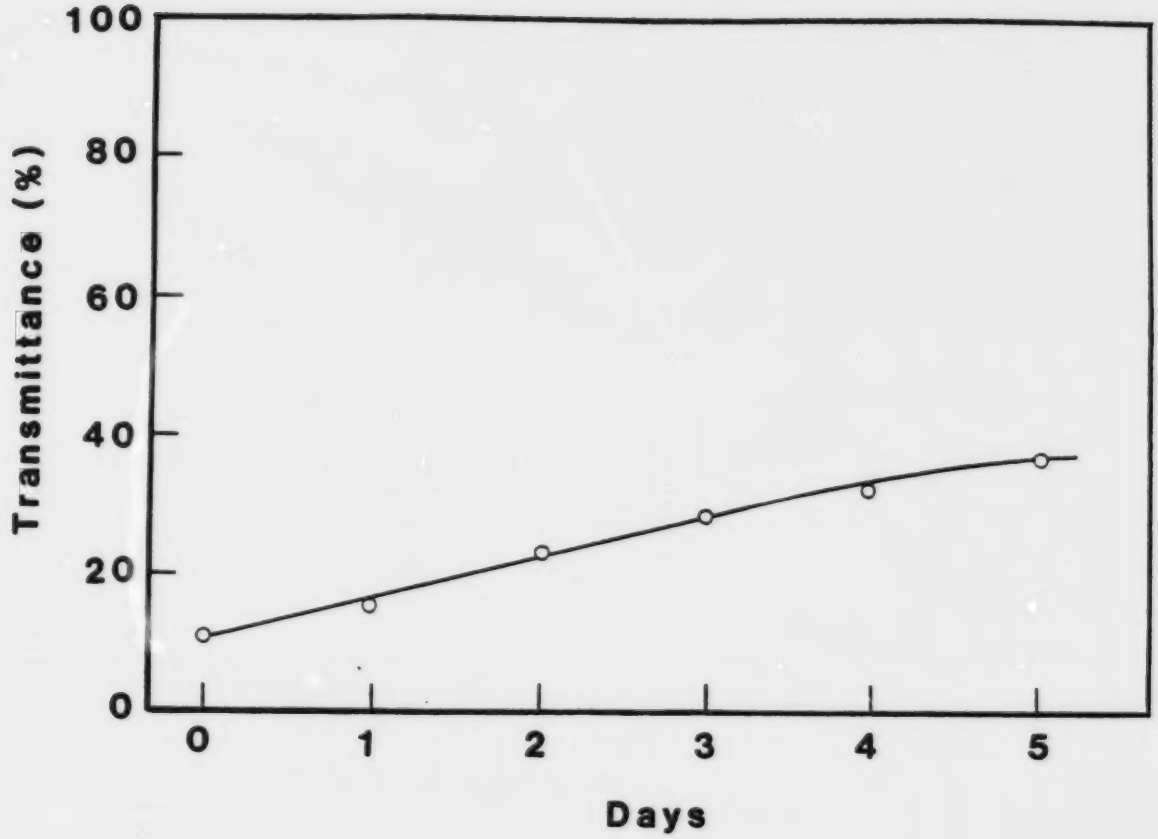


Figure 43. Self-discharge of prototype III.

5.2.4. Prototype IV: ITO/Poly(DPA)/MPEGM-PEGD/WO_3/ITO

The cyclic voltammogram of **Device IV** is shown in Figure 44. Three redox couples are observed between - 0.5 and 1.5 V, corresponding to the oxidation and reduction of WO_3 and Poly(DPA). For Poly(DPA), the oxidation peaks at 0.4 and 0.9 V are related to the polaron and bipolaron formation. In correlation with these redox peaks, **Device IV** exhibits multiple and reversible colour changes from pale yellow at - 0.5 V to deep blue at 1.5 V.

Transmission spectra of **Device IV** at different applied voltages between the bleached state (-0.5 V) and the coloured state (+ 1.5 V) are shown in Figure 45. The response time of **Device IV** is quite acceptable when the applied voltage is switched between 1.5 and - 1.5 V (transmittance between 83 and 13 %) as shown in Figure 46. The device was left at room temperature for two days in the bleached state (82 % transmissivity) and in the coloured state and the variation in transmissivity was measured. No significant variation is noticed as can be seen in Figure 47.

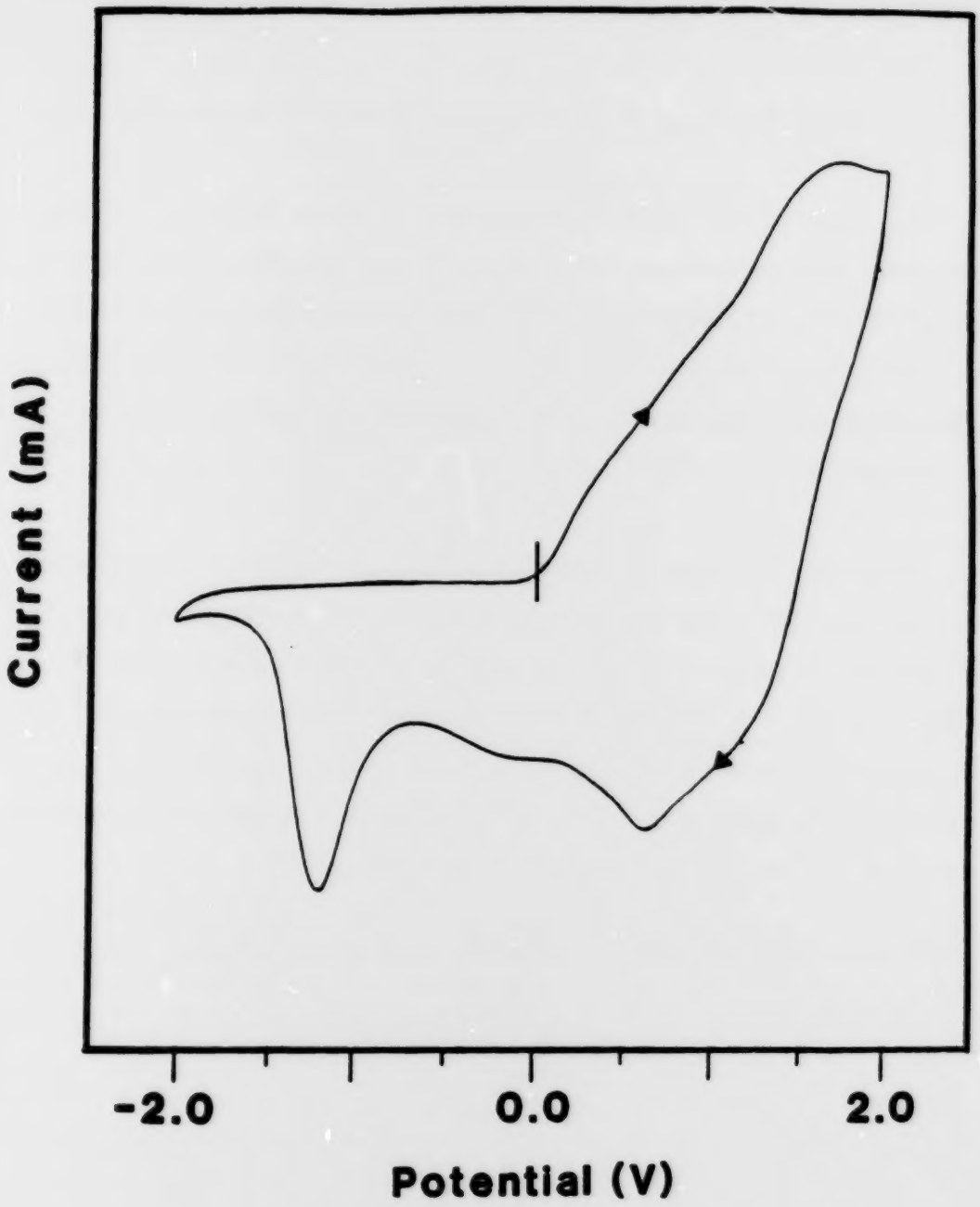


Figure 44. Cyclic voltammogram of prototype IV.

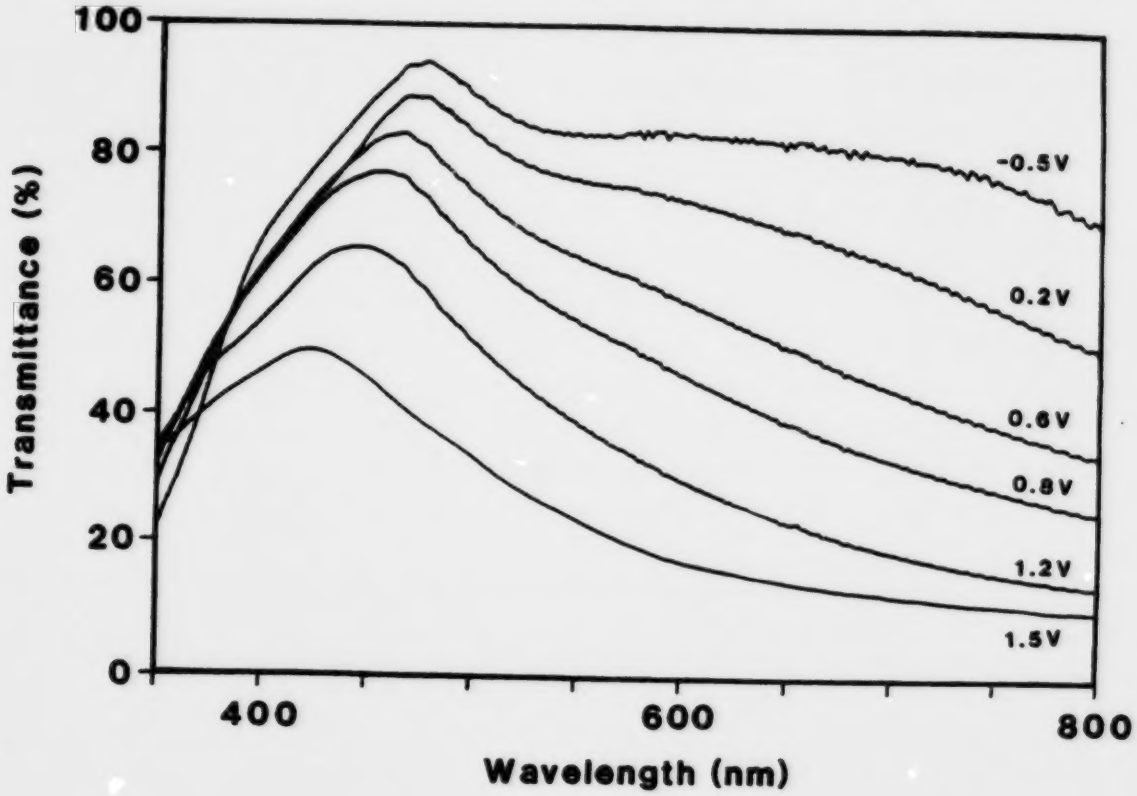


Figure 45. Spectroelectrochemistry of prototype IV.

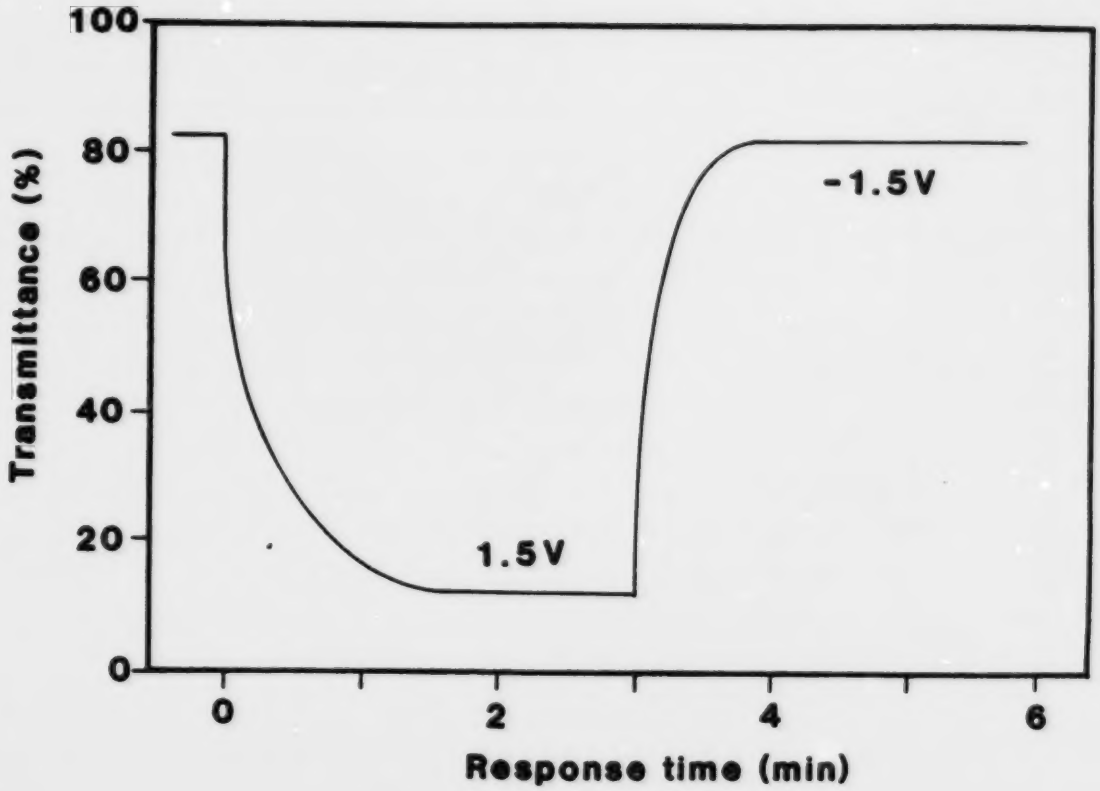


Figure 46. Switching response time of prototype IV.

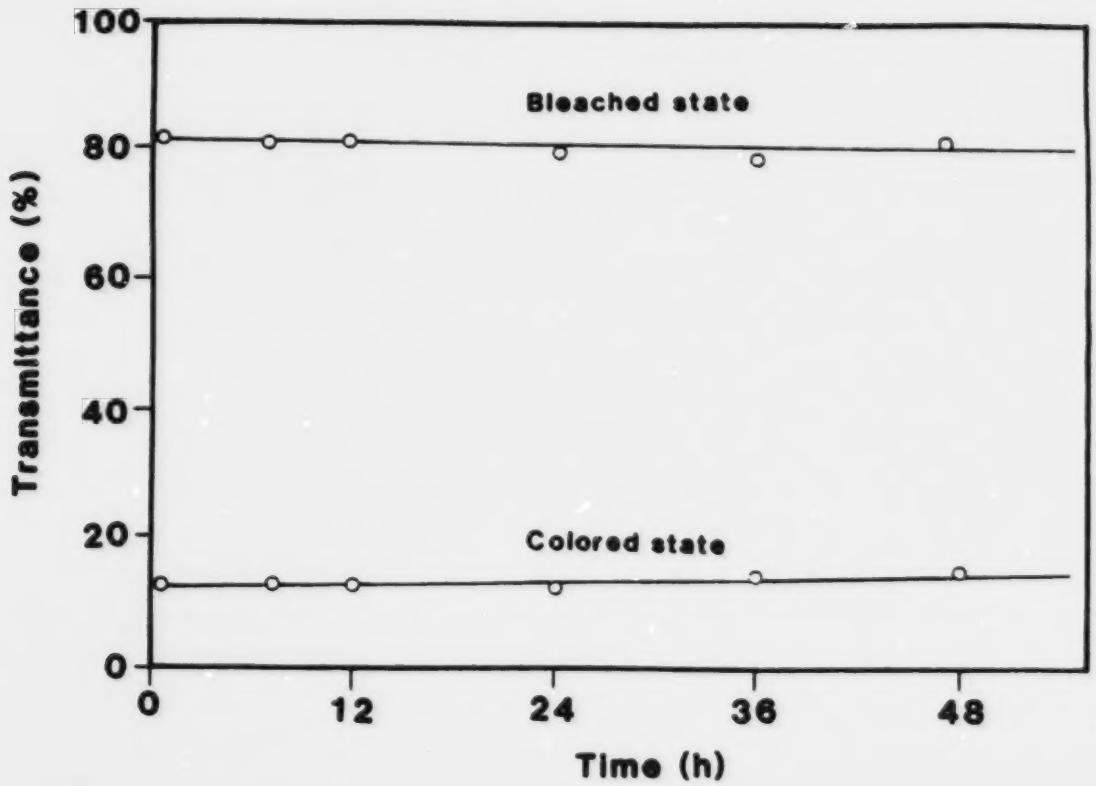


Figure 47. Stability of prototype IV.

CONCLUSION

EC windows, besides a net energy benefit, are also providing design options for commercial builders, and for interior architects and designers.

At the present state of the art, technological development of an EC window is still a high-risk project for industry (except in Japan), but they are strongly supported by governments (in Canada by EMR). The ultimate acceptance will depend on the demonstration of technical and economic feasibility.

Therefore, our efforts have been oriented towards the development of the ideal multilayer solid-state electrochromic window structure as shown in Figure 1. Our EC window device is based on aesthetically, inexpensive materials and on cost-effective fabrication processes with high potential for economic scale-up.

A wide variety of electrochromically active materials were prepared and characterized in our laboratory.

Coatings deposited to date include anodically electrochromic materials (e.g. conductive polymers) and cathodically electrochromic materials (e.g. transition-metal oxides). Electrodeposition technique suitable for coating large flat glass panels was developed.

Propriety gel and glassy polymer conductive electrolytes were also developed.

All solid-state thin film prototype "smart" windows have been successfully fabricated. 5-layer devices seemed to be the most stable and useful. These prototypes exhibit interesting optical and electrical besides useful electrochromic properties.

We have demonstrate the technical feasibility of our EC window laboratory prototype. We are confident that our approach is one of the most cost-effective one and depending on further development, our design has the potential for economic scale-up and long term stability, besides functionality and aesthetically pleasing.

More tests are necessary and further optimization for building applications and for other applications (e.g. vehicles, displays and sunglasses) are required.

RECOMMENDATIONS

The natural progress of an EC window device is schematically illustrated in Scheme III. We have finished the steps 1) and 2).

Four complementary all solid-state EC window devices with different components have been fabricated. They consisted of one polymer electrolyte layer sandwitched between two electrochromic layers coated on conductive transparent glass electrodes by electrodeposition. With our design, due to the chemical balance and electrochemical reversibility in the device during the bleaching and decoloration cycle (similar to a battery), we have fabricated one of the most stable EC window system in the world with low cost fabrication techniques. Moreover, the proprietary materials developed at INRS-Energie permit a more large variety in the coloration and the contrast of the EC windows, permitting a larger choice and acceptance from the customers.

However, additional works are necessary for the complete evaluation of EC windows, particularly the scale-up and production feasibility. Recently, we have developed new electrochromic materials that are soluble in water and common solvents. Therefore, large surface coating by roll techniques is possible, lowering tremendously the production cost of the EC devices.

Some of the most performing prototypes must be subjected to durability, stability and lifetime testing as shown in Scheme II-3. Those that are successful in step 3) will become candidates for commercialization.

SCHEME III

1) Laboratory Research	Evaluation of materials, components, other variables and complete EC windows
2) Laboratory Prototype (1 ft^2)	Evaluation of complete EC windows from 1) including scale-up and production feasibility
3) Durability of Prototypes	Evaluation of prototypes from 2) under static, real time and accelerated test conditions
4) Commercially Feasible EC Windows	Commercialization Candidates EC windows based on results in 3)

ACKNOWLEDGEMENTS

We desire to gratefully acknowledge the enthusiastic support and encouragement of Mr. Tim Mayo, Coordinator of Solar Energy Development Program, Energy, Mines and Resources Canada.

We wish to acknowledge the interests of Dr. Dobrowolski from the National Research Council of Canada and of Mr. Joel Allarie from E.M.R.

Finally, we would like to thank particularly Dr. P. Verly from NRC for his special interest in this project and for his relevant comments during the redaction of this report.

This project was supported:

- For the fundamental research sub-project by NSERC (operating grant No. OGPIN 004, instrument grants No. EQPEQ 004, strategic grant No. SG-004)

- For the prototype development sub-project by EMRC (contract No. 23283-7-620/01-SS).

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APPENDIX

REPRINT 1

Table 2 Screening factors for PS (star) in PVME

Number of arms	Fraction excluded (K)	Vertical shift (°C)
14	0.21	2.0
18	0.26	1.0
22	0.27	0.0

curves is insignificant when one considers how sensitive the phase diagram for a polymer blend can be to small changes made to the blend system. For example, a 40° elevation in the PS/PVME cloud point curve results from the substitution of deuteropolystyrene of the same molecular weight for conventional PS[10]. Thus the 2° difference obtained for the 14-arm system indicates that star substitution has almost negligible effect on the thermodynamics of polymer miscibility.

The fraction of excluded polystyrene was calculated for each of the three stars by selecting a value of K for which the star PS/PVME cloud point curve superimposes on the PS/PVME cloud point curve (*Figures 3* and *4*). In *Table 2* the values obtained for K as well as the vertical shift necessary for the superposition are presented for all three stars. As one would expect, the fraction of the core that is excluded decreases with star functionality. With the accuracy of the experimentally determined value of K being at best only $\pm 10\%$, it is difficult to consider the precise functional dependence of K on the star functionality f.

Although star-branched polymers have been almost exclusively used as model polymers, the implementation of high functionality branching in the design of novel polymers could be utilized to precisely control the physical properties of a material. In a copolymer, the presence of a region which preferentially excludes a given component could alter both mechanical properties such as toughness and the phase behaviour exhibited. In addition, the tendency of the core region to be accessible to low molecular weight solvents only, opens up the possibility for the application of these materials in areas such as chromatography.

Acknowledgements

We wish to thank the Exxon Education Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society for the support of this research.

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Multicolour electrochromic poly(*N*-naphthylaniline) film

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(*Received 7 October 1988*)

The electrochemical polymerization of *N*-naphthylaniline gave uniform polymer films with good electrochemical response. Poly(*N*-naphthylaniline) film showed reversible and durable multiple colour changes from yellow to red to dark blue in the potential range of 0.5–0.8 V vs. Ag/AgCl.

(Keywords: conductive polymer; polyaniline; electrochromic film)

Introduction

Electropolymerized polyaniline films have received considerable attention owing to their opto-electrical properties and potential applications[1,2]. The electrochromic properties of polyaniline films have been studied for display devices applications[3–10]. It has been reported that an electropolymerized polyaniline film showed reversible multiple colour changes from transparent yellow at −0.2 V vs. SCE to green at 0.5, dark blue at 0.8 and black at 1.0[3–5]. Since polyaniline deteriorated upon exposure to potentials higher than 0.6 V in acidic aqueous solution, it is necessary to lower the upper limit potential as much as possible (to 0.4 V, green colour) to get durable repetitive cycles but at the expense of colour range and contrast. Our interests in solid-state batteries and electrochromic devices led us to investigate the electrochemical and chemical polymerization of several aromatic ring and nitrogen-substituted aniline derivatives[8–14]. We have already reported the influence of alkyl and aryl substituents of aniline on the electrochromic properties of some poly(substituted anilines)[8–12]. In this communication, we present the electrochemical polymerization of *N*-naphthylaniline and the electrochromic properties of this new and stable polymer.

Experimental

The electrochemical polymerization was carried out in a one-compartment cell using platinum foils (1 cm^2) as working and auxiliary electrodes. The electrochemical potentials were recorded *versus* a double junction Ag/AgCl/KCl (3.8 M) electrode. For spectroelectrochemical measurements, an indium tin oxide (ITO) conducting glass (Applied Films, 20 ohms/square) was used as the working electrode. Solutions of 0.1 M *N*-

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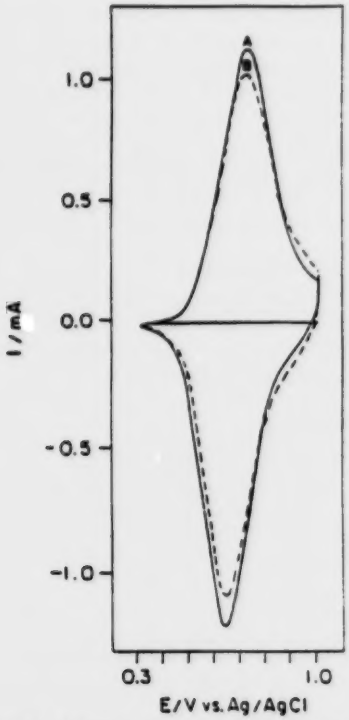

Figure 1 Cyclic voltammograms of poly(*N*-naphthylaniline) film in 1 M $LiClO_4$–CH_3CN after: (A) 1 scan; (B) 200 scans

naphthylaniline and 1.0 M $LiClO_4$ in acetonitrile were electrolysed potentiostatically at 0.65 V leading to a red–violet polymer film on the platinum electrode. Thin films on ITO electrode were obtained by applying a potential of 0.8 V. After its synthesis, the poly(*N*-naphthylaniline) film was rinsed with copious amounts of acetonitrile in order to remove low molecular weight species and excess monomer.

Results and Discussion

Figure 1 shows cyclic voltammograms of the poly(*N*-naphthylaniline) film (1.6 μm thick) in a 1 M $LiClO_4$–CH_3CN solution after 1 (curve A) and 200 scans (curve B). One broad and symmetrical oxidation peak is observed at 0.73 V which is only 0.03 V lower than the monomer oxidation potential (0.76V). This feature can be explained by the weak electronic delocalization in the polymer chain due to a non-planar conformation between phenyl and naphthyl groups[12]. In effect, it was shown that *N*-arylanilines polymerized, not by a head-to-tail mechanism as observed for polyaniline, but by a 4-4' coupling mechanism implying the insertion of the aryl group in the polymer backbone[12–14]. Only a small change in the current intensity was observed in the voltammogram shape after more than 200 cycles between 0.3 V and 1.0 V. The good 'cyclability' of the poly(*N*-naphthylaniline) film is probably due to the highly porous structure of the polymer which provides a large contact surface with the electrolyte and efficient self-exchanges of electrons.

The polymer film on ITO exhibits multiple colour changes (yellow–red–purple–dark blue) when the potential is cycled between 0.0 V and 0.8 V vs. Ag/AgCl as shown in the absorption spectra (*Figure 2*). At 0.0 V, the yellow film in the reduced form presents a visible absorption spectrum with only one absorption band at 382 nm. This absorption peak can be related to the transition between the valence and the conduction bands and hence to the band gap[13]. When the applied potential is increased to 0.6 V, the polymer film turns red with a new absorption band at 540 nm. At 0.7 V, the polymer film becomes purple and this is followed by a simultaneous increase and widening of the 540 mm band. A dark blue film is obtained when the potential reaches 0.8 V and the spectrum shows a broad band that covers practically the whole visible spectral range. Concurrent with these modifications, the 382 nm band decreases in intensity and shifts to higher energies. These new peaks in the visible region can be related to the formation of polarons[8]. The most striking point is in the fact that all colours from yellow to dark blue are reversibly obtained in a very small range of only 0.3 V between 0.5 V and 0.8 V vs. Ag/AgCl, corresponding to the single peak observed in cyclic voltammetry (*Figure 1*). As far as we are aware, this phenomena is unique for conducting polymers. Poly(aniline) also exhibits multiple colour changes (pale yellow–green–dark blue) over a large potential range between −0.2 V and 0.8 V vs. SCE but irreversible degradation occurs when the potential is raised above 0.6 V[3–7].

Conclusions

In summary, uniform and stable poly(*N*-naphthylaniline) films showing good electrochemical and electrochromic properties can be prepared electrochemically in acetonitrile. No significant modification has been observed in the cyclic voltammogram after 200 cycles between 0.3 V and 1.0 V vs. Ag/AgCl in 1 M $LiClO_4$–acetonitrile solution. Upon cycling the potential between 0.5 V and 0.8 V, poly(*N*-naphthylaniline) film shows multiple and reversible colour changes (yellow–red–dark blue). Reproducible doping and undoping by electrochemical methods has been demonstrated, suggesting potential applications of this new conductive polymer to electrochromic devices.

Acknowledgements

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and contracts from Energy, Mines and Resources Canada (Solar Energy Development Program). J.G. is grateful to FCAR for a graduate fellowship.

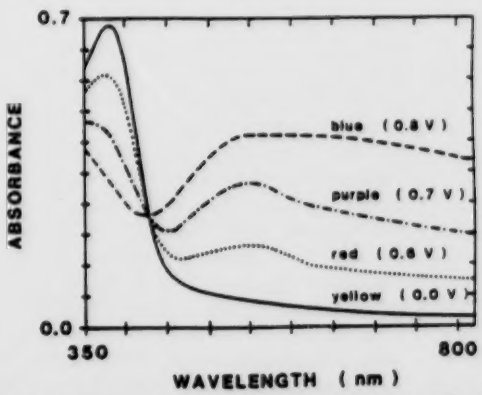

Figure 2 Absorption spectra of a poly(*N*-naphthylaniline) film dipped in 1 M $LiClO_4$–CH_3CN at various applied voltages

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Spectrophotometric measurement of birefringence and its application to aramid fibres

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(Received 14 October 1988)

Application of the spectrophotometric method for the measurement of the birefringence of aramid fibres is reexamined. Literature data are shown to be systematically overestimated.

(Keywords: aramid; Kevlar®; birefringence; spectrophotometry)

Compensation techniques are the most common methods for measuring birefringence (Δn). They are limited, however, to a rather small optical path difference (OPD) range because the wavelength dispersion characteristics of the compensator crystal generally do not match those of the specimen, thereby introducing a systematic error. As the OPD increases, due to a thick specimen and or high birefringence, this error increases correspondingly. This problem, sometimes referred to as 'fringe jumping', was recognized by Airy[1] as long ago as 1833 and discussed many times since, notably by Faust and Marrinan[2]. In 1951, Rittman[3] proposed a spectroscopic method to determine an 'apparent' birefringence; a dispersion correction factor was applied to obtain the true birefringence. A modern version of the same technique was introduced a few years ago by Yang *et al.*[4], for application to fibres. These authors, and, more recently, Hartshorne and Laing[5], arrived at surprisingly high values of birefringence for some specimens, particularly for aramid fibres. For example, values in the range 0.6–0.87 were quoted for a wavelength (λ) of 600 nm. These values are considerably at odds with the 0.42–0.54 range usually reported from direct measurement of the refractive indices by interference microscopy[6–8]. Such discrepancies go well beyond usual experimental error and suggest dispersion effects, known to be prominent for high refractive index materials[9], as is the case for aramid fibres. The modern spectrophotometer technique is reexamined here.

In the spectrophotometric method, the specimen is placed between crossed polarizers and oriented with its optic axis (fibre axis) at 45° to the polarization directions. The variation of the transmitted intensity is recorded while continuously changing the wavelength. Minima of intensity occur when the OPD is a multiple of λ, so that the constitutive equation is:

$$\text{OPD} = m\lambda = \Delta n d \qquad (1)$$

where m is the order of interference and d the fibre diameter. In the papers discussed above, the birefringence was deduced from the slope of a plot of m as a function of $1/\lambda$. Obvious dispersion effects were recognized in the non-linearity of the resulting curve. They were minimized by measuring the birefringence at high λ only (where the relationship is more linear[4]), or by fitting a polynomial to the data, whose derivative was taken as the OPD[5].

In this analysis, we elect to represent dispersion effects in the form of the Cauchy expression, widely used for the refractive indices of immersion oils[10] and generalized here to birefringence. For simplicity the expression is here written to the fourth order only in $1/\lambda$, so that the birefringence is expressed as

$$\Delta n = a + b/\lambda^2 + c/\lambda^4 \qquad (2)$$

where a and b are constants typical of the material.

Inserting (2) into (1) now gives

$$m = d(a + b/\lambda^2 + c/\lambda^4)(1/\lambda)$$
$$m = d(a/\lambda + b/\lambda^3 + c/\lambda^5) \qquad (3)$$

and the slope of the curve of m vs. $1/\lambda$ is

$$\text{slope} = d(a + 3b/\lambda^2 + 5c/\lambda^4)$$

or, from the expression of Δn in (2),

$$\text{slope} = d(\Delta n + 2b/\lambda^2 + 4c/\lambda^4) \qquad (4)$$

The birefringence obtained from the slope overestimates the actual value by a factor $(2b/\lambda^2 + 4c/\lambda^4)$ so that one can write:

$$\Delta n = \Delta n_{app} - 2b/\lambda^2 - 4c/\lambda^4 \qquad (5)$$

where Δn_{app} is the apparent birefringence. This expression

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REPRINT 2

J. Electroanal. Chem., 274 (1989) 135–142
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Formation of poly(4-phenylaniline) by electropolymerization of 4-aminobiphenyl or diphenylamine

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(Received 10 March 1989; in revised form 4 August 1989)

ABSTRACT

4-Aminobiphenyl and diphenylamine were electropolymerized in acidic and organic media to produce poly (4-aminobiphenyl) and poly (diphenylamine), respectively. The resulting polymers present similar cyclic voltammograms and FTIR spectra. 4-aminobiphenyl undergoes the usual C–N head-to-tail coupling while diphenylamine follows a 4,4′ C–C phenyl–phenyl coupling.

INTRODUCTION

Polyaniline, Poly(I), has received considerable attention recently because of its good chemical stability and electrical conductivity [1]. This polymer, which can be prepared either as thin films by electrochemical oxidation or as a powder by the chemical oxidation of aniline in aqueous acid media [2], results from head-to-tail coupling between oxidized aniline species [3]. However, this polymer like many other conducting polymers, is not soluble in common organic solvents because of the stiffness of its backbone. The incorporation of substituents in the polymer skeleton is a common technique for the preparation of soluble polymers and this concept was applied successfully to poly(thiophenes) [4]. For Poly(I), different substituents can be attached to the nitrogen or the aromatic ring. Therefore, anilines with alkyl [5] and aryl [6] groups on the aromatic ring, and alkyl [7], benzyl [8] and aryl [9] substituents on the nitrogen have been successfully polymerized. Because of the preferential head-to-tail polymerization mechanism, only anilines with aryl substituents on the position 4 (*para*) can be polymerized [6]. Previous studies of the polymerization of 4-aminobiphenyl have shown the formation of a conductive

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polymer film intermediate between polyaniline and poly(*p*-phenylene) [6]. Electrochemical synthesis of poly(diphenylamine), Poly(II), was also reported [10,11] and although the head-to-tail coupling mechanism was discounted based on steric reasons [10], no clear evidence of the actual mechanism was provided.

In this paper we report the results for the synthesis and characterization of polymeric conductive films obtained by the electrochemical oxidation of 4-aminobiphenyl and diphenylamine. We present electrochemical and spectroscopical data that show the resulting polymers are similar.

EXPERIMENTAL

Diphenylamine and 4-aminobiphenyl were obtained from Aldrich Co. and used without further purification. Reagent grade hydrochloric acid (Fischer Scientific Co.), lithium perchlorate (Aldrich) and HPLC grade acetonitrile (Caledon) were also used as received. Films of poly(4-aminobiphenyl), Poly(III), were obtained from solutions containing 0.02 M 4-aminobiphenyl in a mixture of 2.0 M hydrochloric acid and acetonitrile (68 : 32 v/v), on platinum electrodes by applying a constant potential of 0.9 V versus SCE for 10 s. The resulting films were washed with CH_3CN. Films of poly(diphenylamine), Poly(II), were prepared by keeping platinum foil electrodes in a solution of 0.1 M of diphenylamine and 1.0 M of lithium perchlorate at fixed potential of 0.8 V (versus Ag/Ag^+ electrode) for 10 min. The polymers obtained were washed with acetonitrile in an ultrasonic bath leaving smooth and uniform films on the platinum electrodes. The film thickness of both polymers has been evaluated to be around 1 μm.

Cyclic voltammograms in acetonitrile were recorded when their shape was stable upon cycling the potential with time. This was usually obtained after the fifth scan. Stable voltammograms of Poly(III) in 2.0 M HCl were obtained after twenty scans. The voltammograms were recorded using a one-compartment cell and a platinum foil as the auxiliary electrode. SCE and Ag/Ag^+ were used as reference electrodes in aqueous and organic media, respectively.

Cyclic voltammograms were obtained with a BAS potentiostat (Model CV-27) and an X–Y recorder (HP-7045A). The infra-red absorption spectra were recorded using a Bomem FTIR (Michelson 100). Spectra were taken at room temperature under nitrogen atmosphere from pressed KBr disks.

RESULTS AND DISCUSSION

Film preparation

The syntheses of Poly(II) and Poly(III) films on Pt were performed by fixed-potential electropolymerization. Poly(II) films were prepared from solutions of diphenylamine in acetonitrile. Poly(III) films were obtained from solutions of 4-aminobiphenyl in a mixture of 2 M HCl + CH_3CN (68 : 32 v/v) [6]. The Poly(III) films were rinsed with CH_3CN, then immersed in a 0.1 M NaOH aqueous solution to deprotonate the acid-doped material fully and finally rinsed with water. For

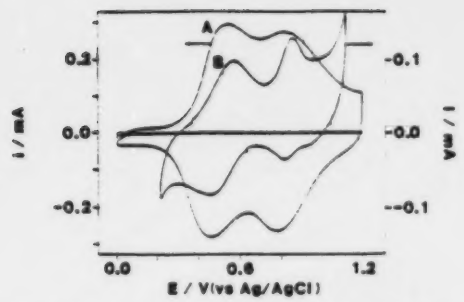

Fig. 1. Cyclic voltammograms of poly(diphenylamine) (A) and poly(4-amunobiphenyl) (B) thin films (1 μm) on Pt in 1 M $LiClO_4 + CH_3CN$. Sweep rate: 50 mV/s.

poly(I) it was observed that protons remained on the chains when the polymer was dipped or cycled in CH_3CN, which influenced strongly the shape of the voltammogram [12,13]. We also noted a shift of the redox potentials to higher values and a change in the voltammogram shape when the polymer films were not washed with an alkaline solution. Therefore, the treatment step with aqueous NaOH solution was necessary to allow the comparison between the unprotonated Poly(II) film obtained from $LiClO_4$ acetonitrile solution and the protonated Poly(III) obtained in acid solution. However, unlike Poly(I) [12,13], Poly(III) films retained their electroactivity in organic media when fully deprotonated (Fig. 1).

Cyclic voltammetry

Figure 1 shows, respectively, the cyclic voltammograms of Poly(II) and Poly(III) films immersed in 1.0 M $LiClO_4 + CH_3CN$ solution at a scan rate of 50 mV/s. The Poly(II) film exhibits two redox couple peaks between 0.0 and 1.2 V vs. Ag/AgCl (Fig. 1A). Their potentials are listed in Table 1. Figure 1B shows the cyclic voltammogram of Poly(III) between 0.2 and 1.1 V vs Ag/AgCl at a scan rate of 50 mV/s. Two redox couples were also observed, and the oxidation and reduction peaks values are reported in Table 1. From these values and the shape of the voltammograms (Fig. 1), it is clear that Poly(II) and Poly(III) films exhibit very

TABLE 1

Redox potentials of Poly(II) and Poly(III) thin films in CH_3CN and HCl

Polymer	Solvent	E_{pa1}/V	E_{pa2}/V	E_{pc1}/V	E_{pc2}/V
Poly(II)	CH_3CN	0.54	0.83	0.44	0.77
	HCl	0.59	[a]	0.40	[a]
Poly(III)	CH_3CN	0.56	0.85	0.45	0.80
	HCl	0.66	[a]	0.54	[a]

[a] Peak potential unstable.

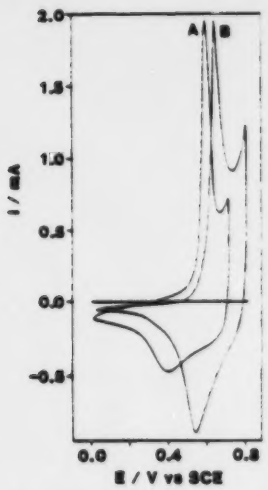

Fig. 2. Cyclic voltammograms of poly(diphenylamine) (A) and poly(4-aminobiphenyl) thin films (1 μm) on Pt in 2 M HCl. Sweep rate: 50 mV/s.

similar redox processes. However, a small difference in the peak sharpness was observed, and assuming that these two polymers are the same, this difference may come from a lower molar mass distribution in poly(III) compared to Poly(II). This, in turn, may indicate that Poly(III) has a lower molar mass than poly(II). This hypothesis is supported by FTIR spectroscopy (see below).

Poly(II) and Poly(III) were also cycled in acidic media. Figure 2 shows their voltammograms in 2 M HCl. As observed in organic media, the two polymer films show similar cyclic voltammograms. Their oxidation and reduction peaks are also listed in Table 1. Three differences can be seen from these values and the voltammograms. Firstly, peak potentials are shifted to more positive values for Poly(III) compared to Poly(II); secondly, the peak to peak separation ($E_{pa}-E_{pc}$) is bigger for Poly(II) than Poly(III) and finally, Poly(III) has the sharpest peak shapes. The same behavior has been observed by Yoneyama et al. when Poly(I) was cycled at different pH values [14]. It was shown that an increase of the electrolyte acidity tends to shift E_{pa} and E_{pc} to higher potential values and to decrease ($E_{pa}-E_{pc}$). They also noted that low pH values gave sharper peaks compared to less acidic media. Since Poly(III) is made in acidic medium and Poly(II) in organic solvent, some differences in environmental acidity of the polymers chains may lead to the modification of the voltammograms. Besides that, molar mass difference may also influence the voltammograms.

Both polymers were stable in acetonitrile up to 1.2 V, but degraded rapidly in 2 M HCl at potential higher than 0.8 V. Moreover, in 2 M HCl, if the potentials were scanned above 1.0 V, new oxidation peaks were formed at around 0.93 V for both

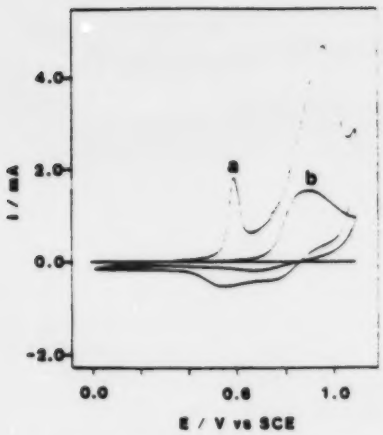

Fig. 3. Cyclic voltammograms of a poly(diphenylamine) thin film (1 μm) on Pt in 2 M HCl with extended upper potential limit: (a) first cycle and (b) second cycle. Sweep rate: 50 mV/s.

polymers. On the next oxidation scan, the current peaks observed at around 0.5 V vanished completely and only the broad peaks near 0.90 V were observed (Figs. 3 and 4). While the origin of the rapid degradation of the polymer films is not yet clear, it is probably due to the instability of the imine group in highly acidic aqueous media, as has been observed many times for Poly(I) [15–18].

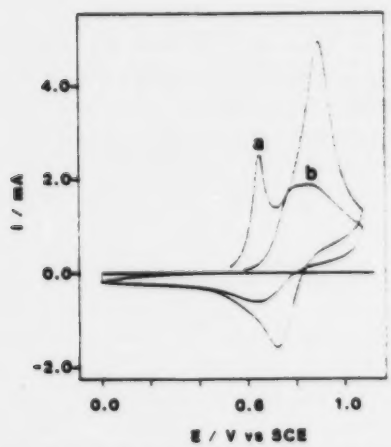

Fig. 4. Cyclic voltammograms of a poly(4-aminobiphenyl) thin film (1 μm) on Pt in 2 M HCl with extended upper potential limit: (a) first cycle and (b) second cycle. Sweep rate: 50 mV/s.

Infra-red spectroscopy

FTIR spectroscopy was also used to compare Poly(II) and Poly(III). Figure 5a shows the spectrum of diphenylamine. Figures 5c and 5b display the FTIR spectra, between 1700 and 400 cm^{-1}, of Poly(II) and Poly(III) prepared in $LiClO_4 + CH_3CN$. Figure 5d exhibits the FTIR spectrum of Poly(III) prepared in HCl. One should note an absorption band near 3400 cm^{-1} for each spectrum which is due to N–H stretching.

Comparing Figs. 5c and 5d, one can see the resemblance between the infra-red absorption of Poly(II) and Poly(III). Each of them shows strong absorption peaks near 1600 and 1500 cm^{-1} that can be assigned to different stretching modes of benzene rings [19–22]. The NH bending of aromatic secondary amines also gives an absorption band in the 1500 cm^{-1} region [23]. Characteristic peaks of doped conducting polymers appear in the region of 1550 cm^{-1} for both Poly(II) and Poly(III) [22,24]. The absorptions bands between 1220 and 1350 cm^{-1} are characteristic of the C–N stretching of an aromatic amine [23]. The peak at 815 cm^{-1} which is characteristic of *para*-disubstitution [22,23], is visible for both polymers but is, of course, absent in the monomer spectrum (Fig. 5a). Note that the presence of this band in the Poly(II) spectrum does not indicate whether the polymer formation comes from the C–N phenyl–nitrogen or the 4,4′ C–C phenyl–phenyl coupling as suggested before [11].

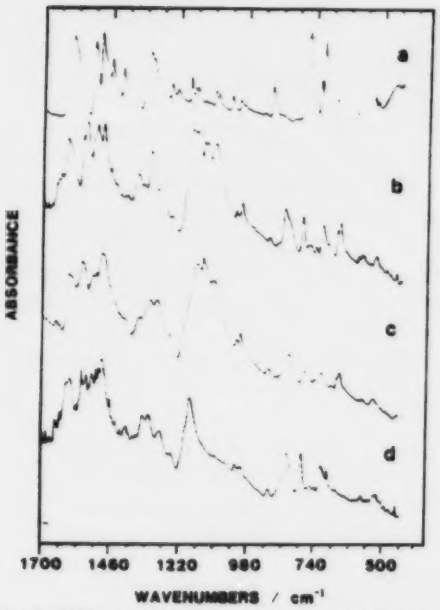

Fig. 5. FTIR absorption spectra of pressed KBr disks of (a) diphenylamine, (b) poly-(4-aminobiphenyl) + ClO_4^-; (c) poly(diphenylamine) + ClO_4^- and (d) poly(4-aminobiphenyl) + Cl.

The band at 690 cm^{-1} is attributed to the CH out-of-plane in phase bending vibration of monosubstituted benzene rings at the ends of the polymers chains [22,23]. If we compare the relative intensities of the bands at 815 and 690 cm^{-1}, we can estimate that the molar mass of Poly(II) (Fig. 5c) is about twice as great as that of Poly(III) (Fig. 5d).

When looking at Figs. 5c and 5d, one can notice a big difference in the region of 1080 to 1140 cm^{-1} and around 630 cm^{-1}. Poly(II) presents many peaks in these regions, but not Poly(III). These differences come from vibrational bands of ClO_4^- [25], which is incorporated in the polymerization of Poly(II), whereas Poly(III) takes Cl^- ions which present no characteristic peaks in that region. To confirm this point, Poly(III) was synthesized in CH_3CN containing 0.1 M of monomer and 1.0 M of $LiClO_4$. The fixed potential electrolysis (0.8 V vs. Ag/Ag^+) leads to a deposit on the platinum electrode. Unfortunately, the deposit was very brittle and exfoliated when it was washed with acetonitrile, therefore, no voltammogram could be recorded. However, its FTIR spectrum was obtained (Fig. 5b) and compared to that of Poly(II) (Fig. 5c). This confirms without doubt that the bands observed at 1080 to 1140 cm^{-1} and around 630 cm^{-1} correspond to ClO_4^- vibrations.

CONCLUSIONS

4-aminobiphenyl (Fig. 6A) and diphenylamine (Fig. 6B) were electropolymerised in acidic and organic media, respectively. The similarities of the resulting polymers were shown by cyclic voltammetry. In addition, Poly(II) and Poly(III) present the same FTIR spectra. Therefore, it is possible to conclude that Poly(III) and Poly(II) are the same polymer (Fig. 6C). This conclusion implies that diphenylamine electropolymerizes via the 4,4′ C–C phenyl–phenyl coupling and 4-aminobiphenyl by the conventional C–N head-to-tail coupling. Moreover, it was estimated that Poly(II) had a molar mass twice that the Poly(III). This difference can be explained by two different electropolymerization mechanisms which lead to more irregular coupling in the case of 4-aminobiphenyl compared to diphenylamine. It is also important to mention that this kind of polymer forms a class of its own, since the phenyl groups are incorporated in the macromolecular chains.

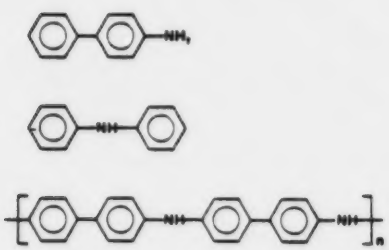

Fig. 6. Structures of 4-aminobiphenyl (A), diphenylamine (B) and poly(4-phenylaniline) (C).

ACKNOWLEDGEMENTS

This work is supported by operating and strategic grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and contracts from Energy, Mines and Resources of Canada (Solar Energy Development Program). J.G. is grateful to FCAR for a graduate fellowship. Additionally, we thank Dr. R. Paynter for useful discussions.

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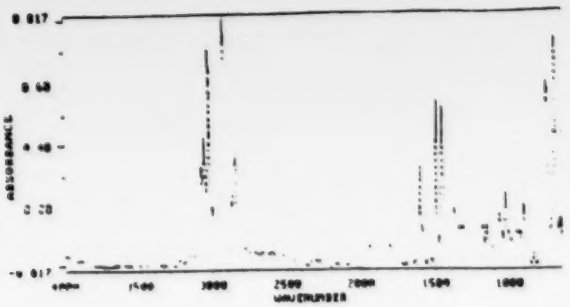

Figure 5 I.r. reflectance spectrum of Resin D with no external lubricant

Figure 4 compares *FT*i.r. microreflectance spectra of three different resin grades of crystal polystyrene (Resins C1, C2 and C3) from the same customer. Each spectrum showed a band attributable to aliphatic carboxylic acid (1705 cm^{-1}), in addition to the polystyrene spectral bands. Residue analysis from the ethanol wash of the resins also indicated a long chain fatty acid which confirms the reflectance analysis. The ethanol wash procedure required 1–2 days as compared to 15 min using the present reflectance approach.

To further validate the procedure, a crystal polystyrene Resin D, which did not contain any external lubricant, was also analysed. No structural features attributable to lubricant type compounds were seen in the spectrum shown in *Figure 5*. The observed bands are due to the resin itself. Microanalysis using an i.r. microscope *FT*i.r. instrument offers a rapid and reliable approach for characterizing fatty acid and fatty acid amide type external lubricants on styrenic polymer surfaces.

Conclusions

A simple, rapid and non-destructive Fourier transform infra-red microreflectance procedure was developed for external lubricant characterization on styrenic resins. This method was successfully applied to several commercial styrene-based resins. It requires little or no sample preparation, and requires very little sample. Rapid lubricant classification significantly reduces the overall quantitative analysis time.

Acknowledgement

Permission to publish this paper has been given by Mobil Chemical Company.

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Poly(*N*-benzylaniline): a soluble electrochromic conducting polymer

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(*Received 14 February 1989*)

Soluble poly(*N*-benzylaniline) was prepared by both electrochemical and chemical polymerization. Besides showing good electrochemical response, electropolymerized and solution-cast films displayed reversible and durable multiple colour changes between 0.0 and 0.8 V *versus* Ag/AgCl.

(Keywords: poly(*N*-benzylaniline); electrochemical and chemical polymerization; soluble; cyclic voltammogram; spectroelectrochemistry)

Introduction

Polyaniline has received considerable attention recently owing to its good electrical, optical and electrochemical properties and its good stability. This polymer can be prepared either as thin films by electrochemical oxidation or as a powder by chemical oxidation of aniline. But like many other conductive polymers, polyaniline is insoluble in most common organic solvents due to the stiffness of its backbone. The incorporation of substituents in the polymer skeleton is a common technique to prepare soluble polymers and this concept is successfully applied to thiophene[1–4]. Therefore, synthesizing polyanilines containing substituted alkyl groups either on the benzenic ring or on the nitrogen atom, is a practical way to enhance their solubility in solvents like acetonitrile, chloroform or tetrahydrofuran[5–10]. In this communication we report the synthesis of soluble poly(*N*-benzylaniline) (PBA) prepared by electrochemical oxidation or chemical polymerization of *N*-benzylaniline in aqueous perchloric acid solution. The cyclic voltammograms, spectral changes and molecular weights of PBA are also described.

Experimental

Poly(*N*-benzylaniline) was prepared by both electrochemical and chemical oxidation of the monomer in aqueous solution of perchloric acid. Electropolymerization of *N*-benzylaniline (Aldrich Chemical Co.) occurred in a solution containing 0.1 M of monomer in 1.0 M of perchloric acid (Aldrich Chemical Co.) using a two-compartment cell. The electrodeposition was done by cycling the potential between 0.0 and 1.0 V *versus* an Ag/AgCl reference electrode. The counter electrode was

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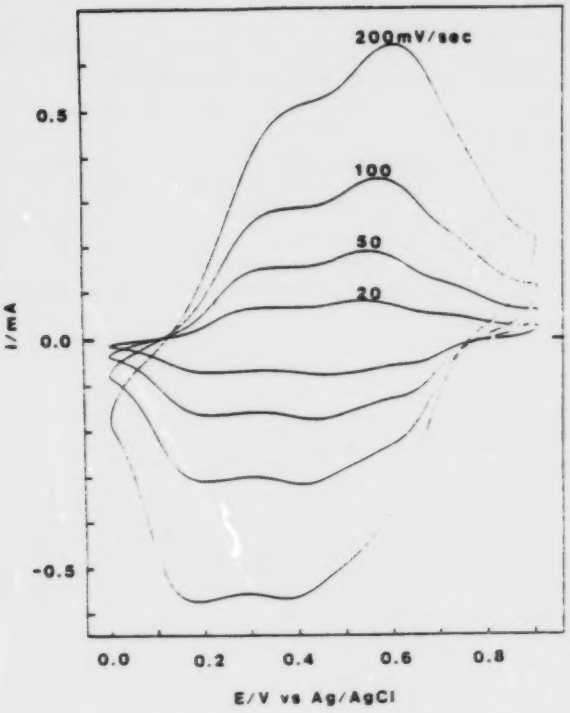

Figure 1 Cyclic voltammograms of a solution-cast poly(N-benzylaniline) film in 1 M perchloric acid at different scanning rates

a platinum foil while the working electrode was an ITO coated glass electrode (Applied Films, 20 Ω square^{-1}) or a platinum foil. The chemical polymerization was done according to a previously reported method[8]. The perchlorate doped polymer powder obtained by either technique was extensively washed with acetone in order to remove all the oligomers and monomer. It was then dried under vacuum and dissolved in acetonitrile. This solution could be used to cast thin films for the electrochemical and the spectroelectrochemical studies. Deep blue uniform thin films on ITO were obtained from diluted solution while films cast from thick solution tend to be brittle. Molecular weight measurements were performed in tetrahydrofuran (THF) or $CHCl_3$ with LC-1 and LC-301 columns (Supelco) and polystyrene standards.

Results and discussion

Figure 1 shows cyclic voltammograms of a poly(*N*-benzylaniline) thin film cast from an acetonitrile solution onto an ITO coated glass electrode in 1.0 M aqueous perchloric acid solution between 0.0 and 0.9 V at four different scanning rates. Thin films of PBA prepared by electropolymerization directly on ITO glass present similar voltammogram shapes. As observed for other poly(anilines)[5–10], two oxidation peaks are observed at 0.3 and 0.6 V, corresponding probably to the formation of polarons and bipolarons[8]. The most noticeable observation concerns the absence of the degradation peak currently reported for the polyaniline[5]. The polymer film is electrochemically stable. No change in the current intensity was observed in the voltammogram shape over 1000 scans between 0.0 and 0.8 V (undoping and doping states) in 1.0 M perchloric acid.

The polymer films on ITO exhibit multiple colour changes (colourless→yellow→green→blue) when the potentials were cycled between 0.0 and 0.8 V *versus* Ag, AgCl as shown in the absorption spectra (*Figure 2*). *Figure 2a* corresponds to the electropolymerized film on ITO glass and *Figure 2b* corresponds to a solution-cast polymer film from an acetonitrile solution. At 0.1 V, no significant absorption was observed at 700–800 nm while a relatively strong absorbance peak was present at 430 nm corresponding to the reductive state of the polymer which is almost colourless. At higher potential, 0.3–0.4 V, the polymer becomes yellow and the absorbance band at 700–800 nm increases as well as the one at 400 nm. At 0.6–0.7 V, the polymer film becomes green as denoted by a very strong absorbance peak in the 700–800 nm region. Finally, at 0.8 V the colour of the film becomes blue while the spectrum shows an increasing absorption band in the 500–600 nm region.

*FT*i.r. studies of electrosynthesized and solution-cast films of PBA in doped and undoped forms, as well as proton and ^{13}C n.m.r. spectroscopy of PBA dissolved in CD_3CN, were also performed[11].

The molecular weights of the perchlorate-doped polymer were investigated by gel permeation chromatography. The THF soluble fraction of the chemically prepared PBA showed an average molecular weight of 25 000 which denotes a high degree of polymerization, while the electrochemically prepared polymer presented a lower average molecular weight (5000). Similar results were observed with poly(alkylanilines)[8].

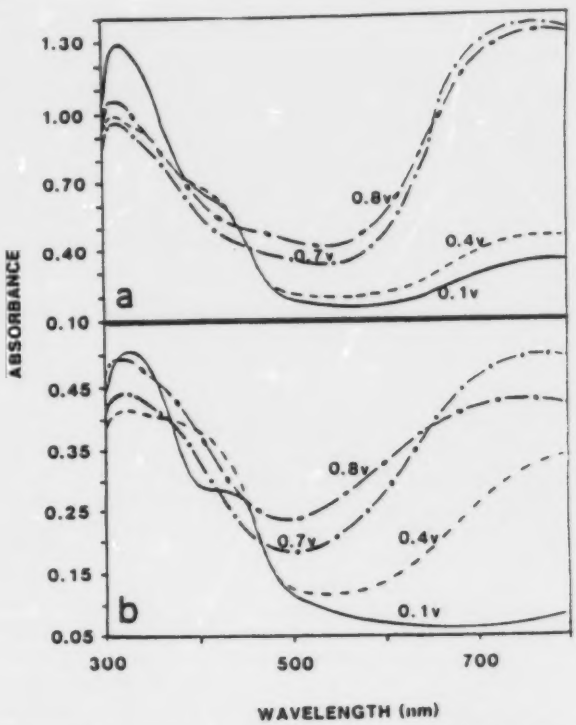

Figure 2 Absorption spectra of (a) electropolymerized and (b) solution-cast PBA films on ITO glass dipped in 1 M perchloric acid at various applied voltages

Conclusion

Poly(*N*-benzylaniline) was prepared by both electrochemical and chemical oxidation of *N*-benzylaniline in perchloric acid. The perchlorate doped polymer is soluble in common organic solvents (e.g. CH_3CN, THF, $CHCl_3$). Electropolymerized and solution-cast films show multiple and reversible colour changes between 0.0 and 0.8 V *versus* Ag/AgCl. Reproducible doping and undoping by electrochemical techniques have been demonstrated, suggesting potential applications of this new processable conductive polymer for electrochromic devices[11,12].

Acknowledgements

This work is supported by operating and strategic grants from the Natural Sciences and Engineering Research Council of Canada and by contracts from Energy, Mines and Resources Canada (Solar Energy Development Program).

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Enhancement at low salt concentration of the efficiency of intermolecular non-radiative singlet energy transfer in labelled poly(L-lysine)

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The fluorescence produced by excitation at 468 nm has been studied in dilute aqueous solutions of ionized poly(L-lysine) chains labelled with a small number of fluorescent probes. Some of the chains are lightly labelled with fluorescein, and the other chains are lightly labelled with rhodamine b. Non-radiative singlet energy transfer from fluorescein to rhodamine b becomes more efficient as the concentration, C, of sodium chloride is reduced. The efficiency is an order of magnitude more sensitive to salt concentration for C in the range 0.002–0.02 M than for C in the range 0.02–0.2 M. This observation is consistent with the development of a loose temporal cooperation of the highly charged poly(L-lysine) chains at low ionic strength, as proposed previously by others, based on the behaviour of the diffusion coefficients measured by dynamic light scattering.

(Keywords: fluorescence; Forster transfer; ordinary–extraordinary transition; polyelectrolyte; poly(L-lysine))

Introduction

The experimental behaviour described as the 'ordinary–extraordinary transition' was first reported a decade ago by Lin *et al.*[1]. Dynamic light scattering was used to monitor the apparent diffusion coefficient of ionized poly(L-lysine) as a function of the concentration of added salt. The 'transition' was detected as an increase, followed by a large decrease, in the apparent diffusion coefficient in a series of measurements performed with decreasing concentration of the added salt and constant concentration of the poly(L-lysine). Subsequently, this phenomenon has been detected by quasi-elastic light scattering with[2] and without[3,4] the presence of a sinusoidal electric field, low shear viscometry[5], X-ray scattering[6], and electrophoretic light scattering[7,8]. While the phenomenon has been detected with several experimental techniques, its occurrence is most dramatically apparent in the diffusion coefficients measured by dynamic light scattering.

There is no doubt about the existence of the phenomenon, but its molecular origin has not been conclusively established. It may arise from a sharing of counter ions by loose temporal aggregates of the polyelectrolyte under conditions where the concentration of the counter ion is small[4]. Small angle X-ray scattering has a peak at a position that implies an intermacro-ion distance of 6–10 nm[6]. An interchain separation in this range suggests that the 'ordinary–extraordinary transition' should be detectable in measurements of the efficiency of non-radiative singlet energy transfer (Forster[9] transfer) with appropriately labelled samples of poly(L-lysine). The experiment requires the presence of a few Forster donors on some of the poly(L-lysine) chains, and the presence of a few Forster acceptors on the remainder of the poly(L-lysine) chains. If the transition induced by lowering the concentration of the added salt leads to cooperative motion of two or more poly(L-lysine) chains, and if this cooperative motion brings donor–acceptor pairs to within a distance less than about twice their Forster radius, the decrease below

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Vol. 136, No. 8, August 1989
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Electrochromic Molybdenum Oxide Thin Films Prepared by Electrodeposition

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Transition metal oxides (e.g. WO_3, MoO_3, V_2O_5 etc.) have recently received much attention owing to their interesting electrical, optical and electrochromic properties [1]. The electrochromic phenomenon is based on the ability of certain materials to change their light-absorbing properties while under the influence of an applied electrical field. This phenomenon is particularly interesting in view of its application in display and "smart window" devices [1]. Among these oxides, WO_3 has attracted the most attention. However, recent work seems to indicate that the electrochromic response of the molybdenum oxide is also aesthetically superior to other electrochromic materials because it absorbs light more uniformly and appears more neutral in color [2]. Transition metal oxides thin films have been prepared by various methods including thermal or electron beam evaporation, RF sputtering [3,4]; chemical vapor deposition, spray, sol-gel and spin coating [5-8]; and recently for WO_3, oxidation of tungsten metal [9] and electrodeposition from tungsten-hydrogen peroxide solution [10].

In this communication, we report the first preparation of molybdenum oxide thin films by electrodeposition and the effect of the heat treatment on their electrochromic properties.

The electrochemical cell used was a standard three-electrode system. Indium tin oxide (ITO) conducting glass (Applied Films, 20 Ω/s) and platinum foil were used as working and counter electrodes, and Ag/AgCl(3.8 M KCl) as a reference electrode. A PAR Model 372 potentiostat and an HP Model 7005B X-Y plotter were used for electrochemical measurements. The spectroelectrochemistry studies were carried out with a Philips Model PU8620 spectrometer.

The deposition solution was prepared by dissolving 1 g of molybdenum foil in 6 ml of hydrogen peroxide (30 %). When the metal was completely dissolved and the exothermic reaction had ended, the solution volume was brought up to 100 ml with distilled water. Deep blue, uniform thin films (0.5-0.8 μm) on ITO glass (5x5 cm^2) were obtained after 3 to 5 minutes by applying a fixed potential (- 10 mV) or by cycling the potential between 0 mV and - 20 mV (scanning rate of 50 mV/sec). Applied potentials more negative than - 200 mV produced electrochemically inactive brown films. Thicker films were obtained with longer deposition time, but cracks appeared when the films were dried. The blue films were copiously washed with distilled water and air dried. Heat treatments were carried out at several temperatures between 130 °C and 450 °C in air for 1 hour.

Cyclic voltammograms in 1 M $LiClO_4$/propylene carbonate (PC) at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s and 4. 20 mV/s) between - 0.5 V and 2.5 V vs Ag/AgCl for an as-synthesized MoO_3 film and a heat-treated film (130 °C, 1 hr), are shown in Figures 1a and 1b, respectively. As noticed before for WO_3 [10], only well-resolved anodic peaks are observed. Heat-treated films sharpen the oxidation peak shape but have no effect on the reduction peak shape. In correlation with the redox process, MoO_3 films exhibit multiple and reversible color changes from lightly colored to dark blue between - 0.5 V to 2.5 V. The heat-treatment also affected the reversibility and the electrochromic properties of molybdenum oxide films as shown in Figure 2. When heated to 130 °C, the film switched from light blue at 2.5 V to deep blue at - 0.4 V (Figure 2a). The film was nearly colorless at 2.5 V when heated to 250 °C, and a good coloration-bleaching contrast could already be obtained between - 0.1 V and - 0.5 V (Figure 2b). MoO_3 films still showed reversible redox and electrochromic behavior when heated up to 350 °C (Figure 2c), but lost all activity at 450 °C (Figure 2d).

In summary, we have shown that uniform and stable molybdenum oxide thin films displaying good electrochemical and electrochromic properties can be prepared by electrodeposition. The

* Electrochemical Society Active Member
Keywords: molybdenum oxide, electrochromic, electrodeposition

electrodeposited films present similar electrochromic behavior to those obtained by other deposition methods [2,4,6]. Upon cycling the potential between - 0.5 and 2.5 V, MoO_3 films exhibit multiple and reversible color changes (pale blue-dark blue). Efforts are presently underway to optimize the deposition method and to study the properties and the stability of MoO_3 thin films for display and smart window applications.

ACKNOWLEDGEMENTS

This work is supported by grants from the Natural Sciences and Engineering Research Council of Canada. We thank Dr. R. Paynter for useful discussion.

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Manuscript received April 7, 1989.
Dr. Le H. Dao assisted in meeting the publication costs of this article.

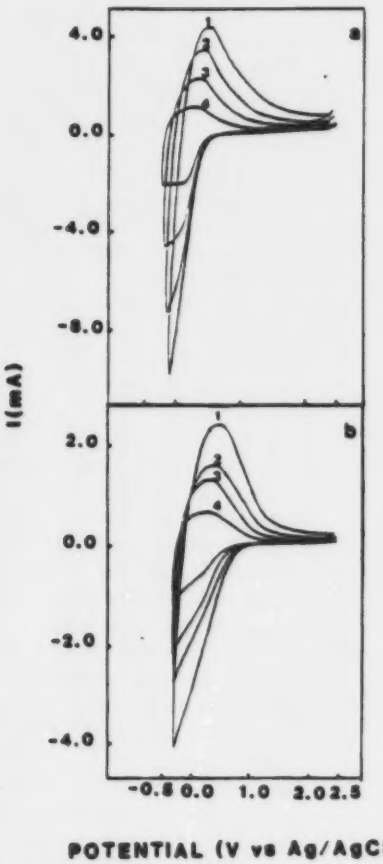

Figure 1. Cyclic voltammograms of a) as-synthesized and b) heat-treated (130 °C) MoO_3 films on ITO glass at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s; and 4. 20 mV/s).

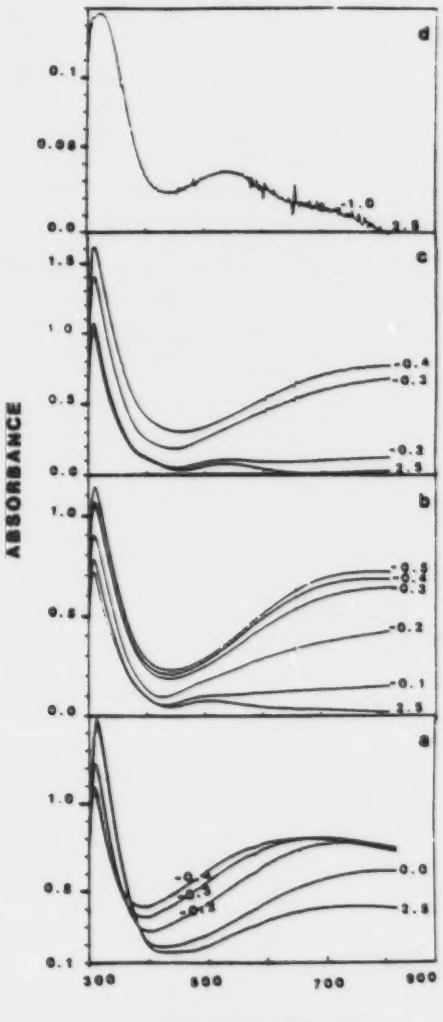

Figure 2. Optical absorption spectra of heat-treated MoO_3 films on ITO (a. 130 °C; b. 250 °C; c. 350 °C; d. 450 °C) at various applied voltages.

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PROCEEDINGS OF THE SYMPOSIUM ON

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PHYSICAL ELECTROCHEMISTRY DIVISION

Proceedings Volume 90-2

THE ELECTROCHEMICAL SOCIETY, INC., 10 South Main St., Pennington, NJ 08534-2896

ELECTROCHROMIC TRANSITION METAL OXIDE THIN FILMS PREPARED BY ELECTRODEPOSITION

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ABSTRACT

Electrochromic transition metal oxide thin films on transparent conducting glass (ITO, Nesa) were obtained by an electrodeposition technique. The deposition bath was prepared by dissolving tungsten or molybdenum or their mixture in hydrogen peroxide. Film characteristics and stability were studied by cyclic voltammetry and spectro-electrochemistry, and compared with those prepared by other techniques. The effects of heat treatment on the film properties are presented.

INTRODUCTION

Electrochromic phenomenon is based on the ability of certain materials to change their light-absorbing properties while under the influence of an applied electrical field. These reversible switching materials permit dynamic control of solar radiation (illumination, glare and heat). This feature is particularly interesting in view of their application in displays and smart window devices.

There are many transition metal oxides that exhibit this phenomenon [1] and the most widely studied is WO_3. However, recent work seems to indicate that the electrochromic response of the molybdenum oxide is aesthetically superior to other electrochromic materials because it absorbs light more uniformly and appears more neutral in color [2]. Transition metal oxides thin films have been prepared by various methods including thermal or electron beam evaporation, RF sputtering [3,4]; chemical vapor deposition, spray, sol-gel and spin coating [5-8]; and recently, oxidation of tungsten metal [9] and electrodeposition from tungsten [10,11] and molybdenum [12] hydrogen peroxide solutions.

We report here the preparation of transition metal oxide thin films by electrodeposition and their electrochromic properties.

EXPERIMENTAL

The deposition solution was prepared by dissolving 1.5 to 3.0 g of metallic W or Mo (powder or foil) in 10 ml of hydrogen peroxide (30 %). When the metal was completely dissolved and the exothermic reaction had ended, the solution volume was brought up to 250 ml with distilled water. The electrochemical cell used was a standard three-electrode system. Indium tin oxide (ITO) conducting glass (Applied Films, 20 Ω/square) and platinum foil were used as working and counter electrodes, and Ag/AgCl(3.8 M KCl) as a reference electrode. Deposited films were copiously washed with distilled water and air dried.

Heat treatments were carried out at several temperatures between 130 °C and 450 °C in air for 1 hour.

A Princeton Applied Research (PAR) Model 372 potentiostat and an HP Model 7005B X-Y plotter were used for electrodeposition and electrochemical measurements. The spectroelectrochemistry studies were carried out in situ with a HP Model 8452 A or a Philips Model PU 8620 spectrometer.

X-ray diffraction patterns were obtained with a Philips diffractometer using a monochromatized CuK_α radiation. The changes of the optical densities of the film were obtained with an He-Ne laser ($\lambda = 633nm$).

RESULTS AND DISCUSSION

Tungsten Oxide Thin films

Dark blue, uniform thin films of WO_3 on ITO glass were obtained by cycling the potential between - 0.4 V and -0.7 V (scanning rate of 50 mV/sec) or by applying a pulse voltage between - 0.5 V and 0.25 V (duty cycle = 80). The films were very fragile and needed a heat treatment for at least one hour at 130 °C before further use.

Figure 1 shows typical cyclic voltammograms for a d.c. electrodeposited WO_3 film on ITO glass cycled at different scanning rates between - 2.0 and 2.0 V vs an Ag/AgCl reference electrode in a 1 M $LiClO_4$/propylene carbonate (PC) solution. As observed before for electrodeposited films [10], only one oxidation peak is observed for WO_3 film. This peak is shifted to higher potential at high scanning rate. When the film is scanned to negative

potential, reduction occurs with injections of both lithium cations and electrons in the film. Hence, lithium tungsten bronze is formed and making the film colored. When the potential is swept to positive value, lithiums and electrons are ejected and the film is bleached.

The electrodeposited WO_3 film was relatively stable in $LiClO_4$/PC open to air when the potentials were cycled between - 1.0 and 1.0 V vs Ag/AgCl (scanning rate of 75 mV/sec) as can be seen in its cyclic voltammogram after a) 1 cycle and b) 3000 cycles (Figure 2).

Figure 3 shows cyclic voltammograms at various applied voltages of a very compact and uniform WO_3 film prepared this time by pulse electrodeposition in the same electrolyte solution. The shapes of the redox peaks of pulsed electrodeposited WO_3 films are sharper and narrower than those obtained for d.c. electrodeposited films. In fact, they are very similar to those obtained for evaporated films [13,14].

Figure 4 shows the relationship between the optical density of the electrochromic film and the injected charge for a pulse electrodeposited film. The slope of the straight line obtained gives the coloring efficiency of the electrochromic film. A high average value of 53 $cm^2\ C^{-1}$ was obtained, confirming by the fact the high quality of the film obtained by pulse electrodeposition. For comparison, coloration efficiency values of 60 and 41 $cm^2.C^{-1}$ were obtained for WO_3 films prepared by evaporation and chemical vapor deposition, respectively [14].

In correlation with the redox peaks, the films changed their coloration with the applied voltages as shown in Figures 5-7. Heat treatment of pulse electrodeposited films affected their coloration efficiency, reversibility and potential coloration-bleaching limits. Figure 5 shows the variation of the absorbance of a WO_3 film heated at 130 °C dipped in $LiClO_4$/PC in function of the applied voltages. Bleached and colored states were obtained, respectively, with potential limits of 1.0 and - 1.0 V. Higher cathodic potentials were necessary to color a film heated to 250 °C (Figure 6). Lower coloration efficiency was observed for film heated up to 400 °C (Figure 7) where dehydration and crystallization of WO_3 films occurred as shown in the X-ray diffraction patterns in Figure 8.

Molybdenum Oxide Thin Films

Deep blue, uniform thin films of MoO_3 on ITO glass were obtained after 3 to 5 minutes by applying a fixed potential (- 10 mV) or by cycling the potential between 0 mV and - 20 mV (scanning rate of 50 mV/sec). Applied potentials more negative than - 200 mV produced electrochemically inactive brown films. Thicker films were obtained with longer deposition time, but

cracks appeared when the films were dried. Contrary to WO_3 deposition, no difference was observed when a pulse voltage was used for the deposition.

Cyclic voltammograms in 1 M $LiClO_4$/propylene carbonate (PC) at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s and 4. 20 mV/s) between - 0.5 V and 2.5 V vs Ag/AgCl for an as-synthesized MoO_3 film and a heat-treated film (130 °C, 1 hr), are shown in Figures 9 and 10, respectively. As noticed before for WO_3 [10], only well-resolved anodic peaks are observed. Heat-treated films sharpen the oxidation peak shape but have no effect on the reduction peak shape.

In correlation with the redox process, MoO_3 films exhibit multiple and reversible color changes from lightly colored to dark blue between - 0.5 V to 2.5 V. The heat-treatment also affected the reversibility and the electrochromic properties of molybdenum oxide films as shown in Figures 11-14. When heated to 130 °C, the film switched from light blue at 2.5 V to deep blue at - 0.4 V (Figure 11). The film was nearly colorless at 2.5 V when heated to 250 °C, and a good coloration-bleaching contrast could already be obtained between - 0.1 V and - 0.5 V (Figure 12). MoO_3 films still showed reversible redox and electrochromic behavior when heated up to 350 °C (Figure 13), but lost all activity at 450 °C (Figure 14).

Contrary to the as-synthesized WO_3 films which are amorphous (Figure 8a), the as-deposited molybdenum oxide films show some crystallinity (Figure 15a). Based on powder diffraction index card No. 12-517, the diffraction pattern corresponds probably to the tetragonal structure of the metastable phase $MoO_{2.8}$ which is known to decompose in MoO_3 on prolonged heating. In effect, when heated to 250 °C, the X-ray diffraction patterns (Figure 15b) indicate that the MoO_3 film is polycrystalline with a predominant orthorhombic crystalline structure in agreement with values from card index No. 5-0508 and those reported for MoO_3 film prepared by vacuum evaporation [15,16].

Tungsten-Molybdenum Oxide Thin Films

WO_3-MoO_3 films were obtained from a mixture of 200 ml of A and 0.1 ml of B. The solution A was prepared by dissolving 3 g W in 10 ml of H_2O_2 (30 %) then brought up to 200 ml with water, and the solution B by dissolving 1 g of Mo in 10 ml of hydrogen peroxide then diluted to 200 ml with water. Addition of larger volume of solution B gave films containing mainly MoO_3. This is due probably to a less cathodic deposition potential of molybdenum oxide and a faster deposition rate compared to tungsten oxide.

The cyclic voltammogram of WO_3-MoO_3 film in 1 M $LiClO_4$/PC (Figure 16a) presents a similar shape than that obtained for WO_3 with a slight

cathodic potential shift for the oxidation peak. The film is very stable and no decrease in the current intensity besides a slight shift in the oxidation peak are observed after 3 thousand scans (scanning rate: 75 mV/sec).

In correlation with the redox process, WO_3-MoO_3 films exhibit reversible color changes from colorless to dark grey. The bleaching and coloration transformation can be seen in the transmittance spectra of a WO_3-MoO_3 film dipped in a 1 M $LiClO_4$/PC solution under various applied voltages (Figure 17). The film is perfectly clear at 0.2 V vs Ag/AgCl reference electrode and turns to light grey at - 0.4 V to dark grey at -0.8 V.

CONCLUSION

In summary, we have shown that stable and uniform transition-metal oxides films having good electrochemical and electrochromic properties can be prepared by electrochemical deposition. The electrodeposited films present similar electrochromic behavior to those obtained by other deposition methods [2,4,6]. Large surface (40 x 40 cm^2) coatings were obtained indicating that the electrodeposition technique is capable of meeting the process and performance required for electrochromic smart window devices.

ACKNOWLEDGEMENTS

This work is supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC).

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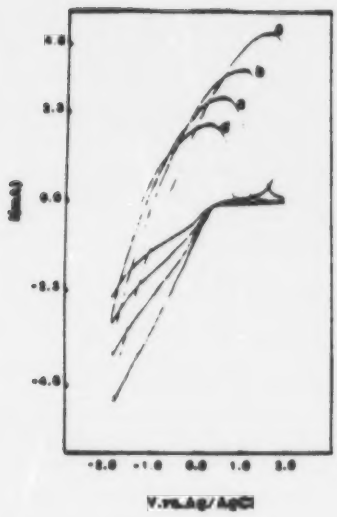

Figure 1. Cyclic voltammogram of WO_3/ITO, prepared by direct current, in 1 M $LiClO_4$/PC at different scanning rates (a. 200 mV/s; b. 100 mV/s; c. 50 mV/s; d. 20 mV/s).

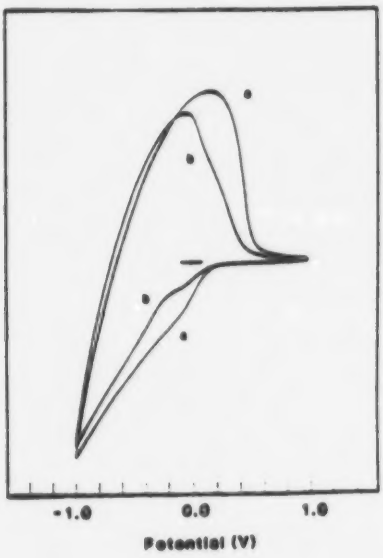

Figure 2.
Cyclic voltammograms of WO_3/ITO in 1 M $LiClO_4$/PC after
a) 1 cycle and b) 3000 cycles.
(Scanning rate: 75 mV/sec)

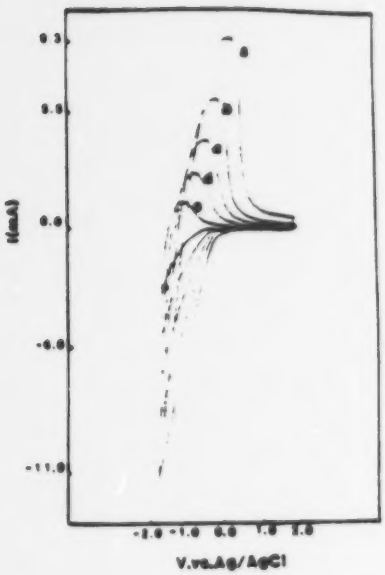

Figure 3.
Cyclic voltammogram of WO_3/ITO, prepared by pulsed current, in 1 M $LiClO_4$/PC at different scanning rates (a. 200 mV/s; b. 100 mV/s; c. 50 mV/s; d. 20 mV/s; e. 10 mV/s).

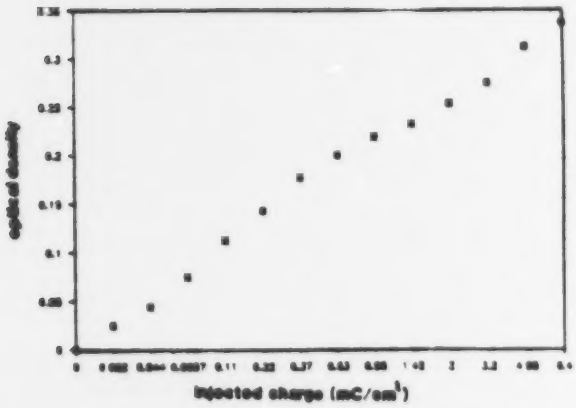

Figure 4. Optical density of WO_3/ITO versus injected charge in 1 M $LiClO_4$/PC.

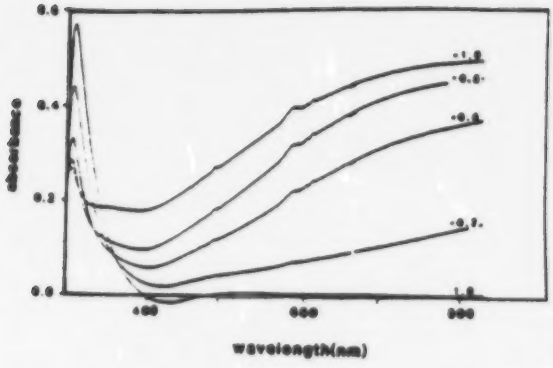

Figure 5. Spectral absorbance of heated (T= 130 °C) WO_y/ITO at various applied voltages.

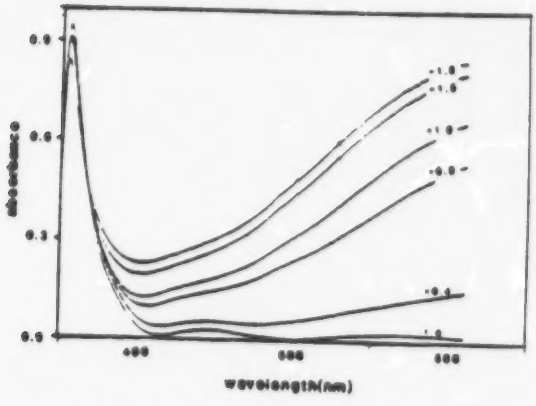

Figure 6. Spectral absorbance of heated (T=250 °C) WO_y/ITO at various applied voltages.

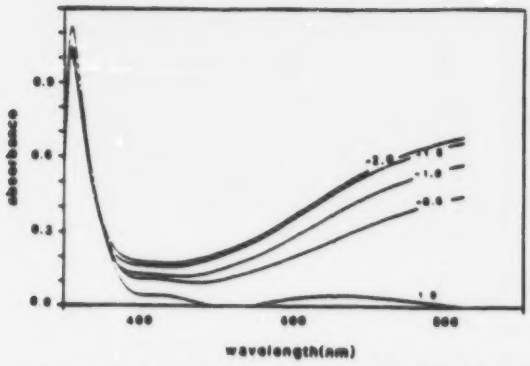

Figure 7. Spectral absorbance of heated (T=400 °C) WO_3/ITO at various applied voltages.

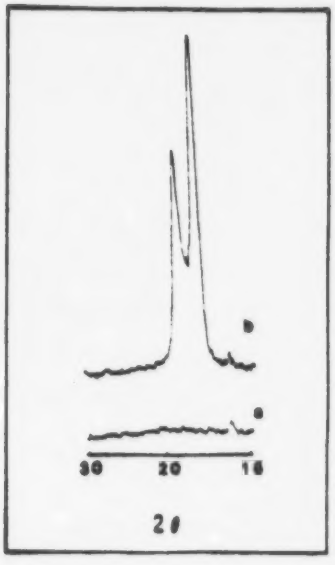

Figure 8. X-Ray diffraction spectra of a) as-synthesized and b) WO_3/ITO heated at T=400 °C

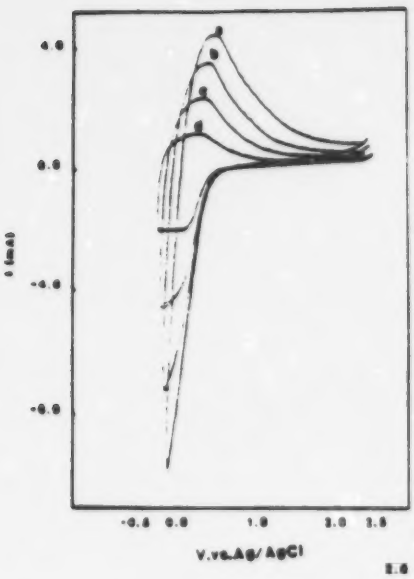

Figure 9. Cyclic voltammograms of as-synthesized MoO_3 films on ITO glass at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s and 4. 20 mV/s).

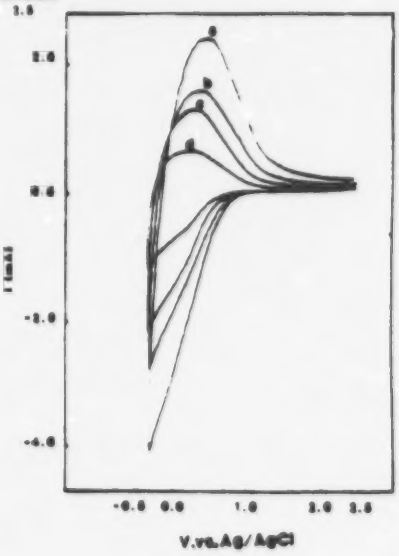

Fig. 10. Cyclic voltammograms of heat-treated (130 °C) MoO_3 films on ITO glass at different scanning rates (1. 200 mV/s; 2. 100 mV/s; 3. 50 mV/s and 4. 20 mV/s).

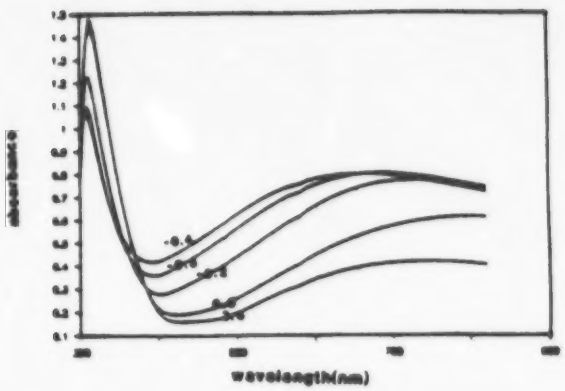

Figure 11. Optical absorption spectra of a MoO_3 film on ITO glass treated at 130 °C at various applied voltages.

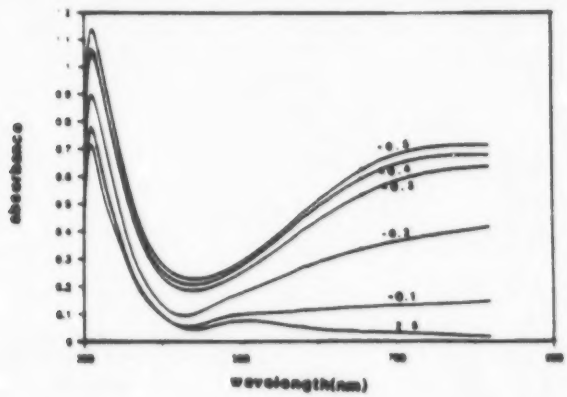

Figure 12. Optical absorption spectra of a MoO_3 film on ITO glass treated at 250 °C at various applied voltages.

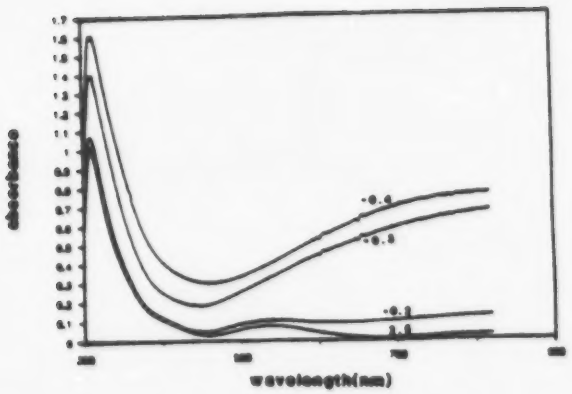

Figure 13. Optical absorption spectra of a MoO_3 film on ITO glass treated at 350 °C at various applied voltages.

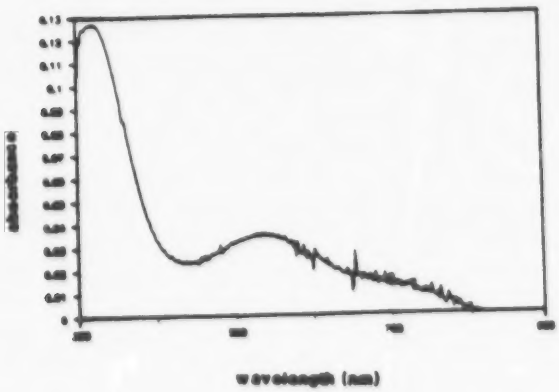

Figure 14. Optical absorption spectra of a MoO_3 film on ITO glass treated at 400 °C at various applied voltages.

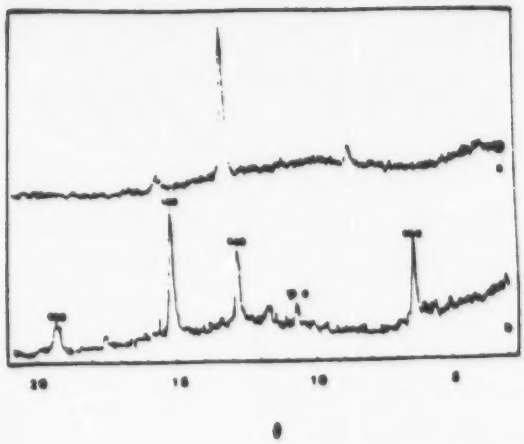

Figure 15. X-Ray diffraction spectra of a) as-synthesized and b) heated (T=250 °C) MoO_3/ITO.

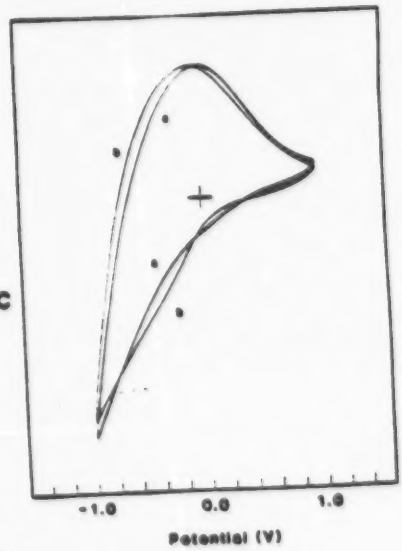

Figure 16. Cyclic voltammogram of WO_3-MoO_3/ITO in 1 M $LiClO_4$/PC (scanning rate 50 mV/s)

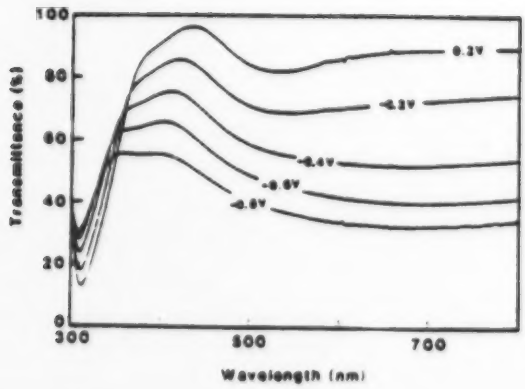

Figure 17. Spectral transmittance of WO_3-MoO_3/ITO in 1 M $LiClO_4$/-PC at various applied voltages.

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Vol. 136, No. 7, July 1989
Printed in U.S.A.
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Poly(N-Benzylaniline)/(Poly(AMPS)/WO_3 Solid-State Electrochromic Cell

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Electrochromic "smart" windows are prospective devices for the control of light transmission in response to the change in brightness of the environment. The basic structure of such a window or electrochromic cell is comprised of three types of thin film materials: a) transparent electrical conductors TEC (e.g. ITO, Nesa) on glass or plastic supports to collect the current, b) electrochromic EC layer films on TEC to form the opto-electroactive elements of the window and c) an ionically conductive electrolyte to separate the two EC films (Figure 1).

A large variety of materials are known to display electrochromism. They may be divided into four general classes : a) transition-metal oxides, b) conductive polymers, c) organic and d) intercalated materials [1]. The bulk of the research published to date have been related to transition-metal oxides (e.g. WO_3, MoO_3, IrO_2 etc.) [1], although many works have been carried out recently on conductive polymers [2,3].

Many electrochromic cells reported in the literature are lacking one or more of the basic components described in Figure 1, resulting in poor long term stability and cyclability. Complementary electrochromic windows, based on cathodically coloring WO_3 and anodically coloring IrO_2 [4] or polyaniline [5], have been fabricated. However, their development is still limited by hight costs of fabrication (vacuum evaporation, sputtering), prohibitive costs of materials (IrO_2) and short term stability of materials (polyaniline).

Extended work has been carried out in this laboratory on developing new low cost electrochromic materials and inexpensive large surface thin film deposition techniques for window applications [3,6,7,8]. We have found that derivatives of polyaniline, which combine sharp color contrast and long term cyclability, are among the best reversible electrochromic materials.

We report here a new solid-state electrochromic cell PPW:

SnO_2/Poly(BAn)/Poly(AMPS)/WO_3/SnO_2

where poly(N-benzylaniline), Poly(BAn), and WO_3 are the electrochromic thin films prepared by electrodeposition and poly(2-acrylamido-2-methylpropanesulfonic acid), Poly(AMPS), the proton conducting polymer electrolyte film.

WO_3 thin films (1-3 μm) were obtained from tungsten-hydrogen peroxide solution on tin-oxide glass (30 ohm/square, 10 x 10 cm^2) in a one-compartment cell using Ni foil and Ag/AgCl (3.8 M KCl) as counter and reference electrodes, by cycling the potential between -400 mV and -800 mV at a scanning rate of 60 mV/s [9,10]. Pulsed plating electrodeposition was also successfully used and high quality films were obtained [10]. The deep blue films were extensively rinsed with water and then thermally treated for one hour at 130°C. Uniform green poly(N-benzylaniline) films were obtained from aqueous solution of 0.1 M N-benzylaniline in 1.0 M phosphoric acid, in a similar cell, by scanning the potential between +400 mV and +800 mV vs Ag/AgCl [11,12]. The two electrochromic electrodes were assembled as shown in Figure 1 with a thin layer of Poly(AMPS) (80 % in water) as electrolyte.

The cyclic voltammogram of the PPW cell is shown in Figure 2c. For comparison, cyclic voltammograms of WO_3 and Poly(BAn) on tin-oxide in Poly(AMPS) with a Ni counter-electrode are shown in Figures 2a and 2b, respectively. No well defined redox peaks were observed for the PPW cell compared to its components. In effect, WO_3 films show the same redox shape as reported in [9] and Poly(BAn) films present two redox couples corresponding to the polaron and bipolaron formation [6,12].

As the applied voltage was varied, the color of Poly(BAn) film reversibly changed from pale transparent yellow in the reduced state (0.0 V vs Ag/AgCl) to dark green in the oxidized state (0.8 V). The WO_3 film also reversibly changed its color from colorless in the oxidized state (0.4 V) to dark blue in the reduced state (-0.8 V) vs Ag/AgCl. Hence, the combined colors of the PPW cell, with Poly(BAn) as working electrode and WO_3 as counter-electrode, changed from transparent clear yellow at -0.1 V to deep blue at 1.0 V as shown in Figure 3.

PPW cells were repetitively cycled more than 10^3 times between the bleached and the colored states

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* Electrochemical Society Active Member

Key Words: electrochromic window, polyaniline, tungsten oxide

without apparent degradation. The cells were also left at room temperature for 16 days in the bleached state (80 % transmittance) and the colored state (20 % transmittance). The variations of the transmittance at 700 nm for the bleached and colored states were followed in the time (Figure 4, curves a and b). The variations in the transmittance observed after many days were mainly due to the degradation of WO_3 by the residual water in Poly(AMPS). Better long term stability was obtained with a non-aqueous solid electrolyte such as poly(ethylene oxide) PEO-$LiClO_4$ system (Figure 4, curves c and d). Other polyaniline derivatives electroactived in organic electrolytes and other solid polymer electrolytes such as polyvinyl alcohol-phosphoric acid, and polysiloxane, polyphosphazene mixed with metal salts, were also studied. These results will be soon reported.

In conclusion, we have shown a new solid-state electrochromic cell with two complementary electrochromic films ,poly(BAn) and WO_3, working in tandem. These results suggested potential applications of inexpensive materials obtained by electrodeposition for electrochromic "smart" windows.

Acknowledgments

This work is supported by grants from NSERC (operating and strategic) and by contracts from EMR Canada (Solar Energy Development Program). Manuscript received Dec. 27, 1989.

Dr. Le H. Dao assisted in meeting the publication costs of this article.

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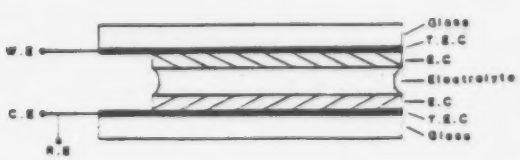

Figure 1. Structure of a complementary electrochromic window.

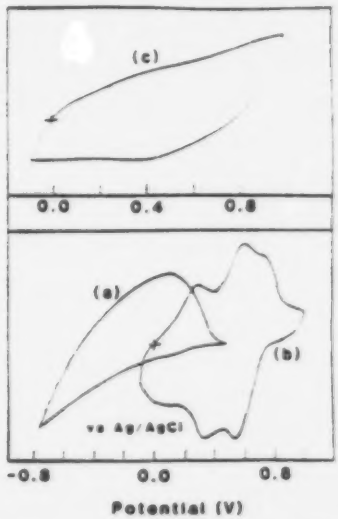

Figure 2. Cyclic voltammograms (50 mV/s) of a) WO_3 film and b) Poly(BAn) film in Poly(AMPS) with a Ni counter-electrode, c) Poly(BAn)/Poly(AMPS)/WO_3 cell

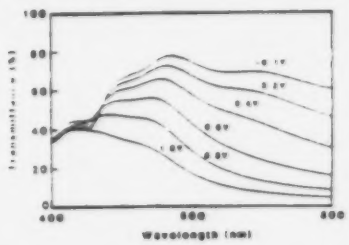

Figure 3. Transmittance spectra of a Poly(BAn)/Poly(AMPS)/WO_3 cell as a function of switching voltage.

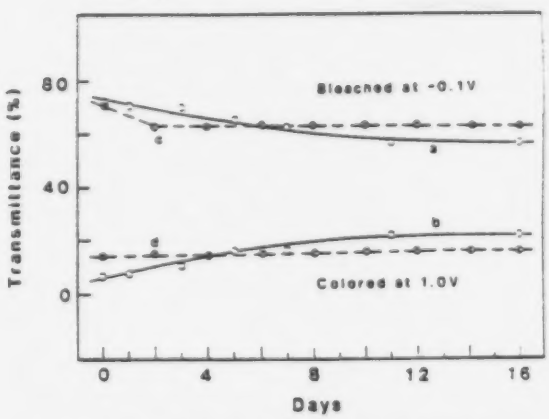

Figure 4. Transmittances in the bleached and colored states, respectively, for Poly(BAn)/WO_3 cells with Poly(AMPS) (curves a and b) and PEO-$LiClO_4$ (curves c and d) electrolytes.

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DESIGN AND OPTICAL MODULATION OF ELECTROCHROMIC WINDOWS

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ABSTRACT

The fabrication and design of electrochromic smart windows based on anodically coloring conductive polymers and cathodically coloring transition-metal oxides are described. Some fundamental and practical aspects of the complementary five-layer transmissive electrochromic devices are presented. The electrochromic layers are prepared by new large surface coating techniques. Solid, gelled or glassy polymers were used as ionically conductive electrolytes . The electrochemical and optical characteristics of all solid-state five-layer electrochromic devices are discussed.

1. INTRODUCTION

Electrochromic smart windows present the prospective to arbitrary control the level of light transmission in response to the change in brightness of the environment. Electrochromism is defined as reversible optical switching of a material to a bleached, colored or intermediate state by the dual ion and electron insertion or removal under an applied voltage. Color centers are created in the material as the result of this injection or ejection, producing optical absorption in the visible and near-infrared wavelength region. These variations in the material optical density are due to both chemical and structural changes.

The basic structure of a transmissive electrochromic device consists of three types of thin film materials: a) transparent electrical conductors TEC (e.g. ITO, Nesa) on glass or plastic supports to collect the current, b) electrochromic EC layer films on TEC to form the opto-electroactive elements of the window and c) an ionically conductive electrolyte to separate the two EC films as shown in Figure 1.

A large variety of materials are known to display electrochromism. They are separated in four general classes : a) transition-metal oxides, b) conductive polymers, c) organic and d) intercalated materials [1]. They are also divided in cathodic and anodic electrochromic materials, depending on the coloration mechanism. The bulk of the research published to date are related to transition-metal oxides (e.g. WO_3, MoO_3, IrO_2 etc.), although many works have been carried out recently on conductive polymers [2,3].

Many electrochromic cells reported in the literature are lacking one or more of the basic components described in Figure 1, resulting in poor long term stability and cyclability. Complementary electrochromic windows, based on cathodically coloring WO_3 and anodically coloring IrO_2 [4] or polyaniline [5], have been fabricated. However, their development is still limited by hight costs of fabrication (vacuum evaporation, sputtering), prohibitive costs of materials (IrO_2) and short term stability of materials (polyaniline).

Extended works have been carried out in this laboratory on developing new low cost electrochromic materials and inexpensive large surface thin film deposition techniques for window applications [6-16].

We report here the design and optical modulation of some new solid-state electrochromic devices.

2. ELECTROCHROMIC SMART WINDOW STRUCTURE

The principles behind the operation of electrochromic windows based on coloring cathode in combination with coloring anode have been discussed in detail previously [15, 17]. The operation of the electrochromic device is such that both layers participate in the coloring and bleaching processes, therefore enhancing the overall efficiency of optical switching. For example, the electrochromic reactions occuring in tungsten oxide cathode and poly(aniline) anode during optical switching are the following:

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$$WO_3 + xM^+ + xe^- \underset{anodic}{\overset{cathodic}{\rightleftharpoons}} M_xWO_3$$

transparent **blue**

$$Poly(An) + xA^- - xe^- \underset{cathodic}{\overset{anodic}{\rightleftharpoons}} Poly(An)A_x$$

pale yellow **blue**

WO_3 film undergoes a transparent to blue modulation on the electrochemical insertion (coloring) or ejection (bleaching) of a cation M^+, typically H^+, Li^+ or Na^+. In the same time, poly(An) modulated between pale yellow to blue on the electrochemical injection (coloring) or extraction (bleaching) of an anion A^-, typically ClO_4^-, $CF_3SO_3^-$.
When the direction of the current flow in tungsten oxide-poly(aniline) electrochromic device is such that the tungsten oxide layer is the cathode and poly(aniline) layer the anode, a dual injection of M^+ in WO_3 and A^- in poly(An) takes place and the electrochromic device develops a deep blue coloration. When the direction of current flow is reversed, the cation and anion are ejected from the electrochromic layers **EC** to the electrolyte reservoir. The electrochromic device returns then to the transparent state.

3. THIN FILM MATERIALS

3.1. Anodic Electrochromic Layer

Extended work has been carried out in this laboratory to develop new anodic electrochromic materials based on conducting polymers (e.g. poly(aniline) derivatives, poly(anthraquinone) styrene or poly(anthraquinone) ethyleneimine [3,6-11]. We have found that electronic conductive polymers based on poly(aniline) are good candidates for the electrochromic anodic layer. Uniform and stable thin films of poly(aniline) with substituents on the aromatic ring or nitrogen were prepared by electropolymerization or by solution casting on transparent conductive electrode. Upon cycling between the potentials limits, multiple and reversible color changes were observed from colorless to black [9,10].

3.2. Cathodic Electrochromic Layer

As reported earlier [12-14], WO_3 films is still the primary candidate for the cathodic electrochromic layer, since it combines robustness with long term stability, although recent work seems to indicate that the electrochromic response of MoO_3 is aesthetically superior [13,18]. We have recently prepared transition metal oxide thin films by electrodeposition [12-14]. Their electrochromic properties compares favorably to those obtained by other deposition techniques.

3.3. Ionically Conductive Electrolytes

Solid, gel and glassy polymers were used as ionically conductive electrolytes. The two electrochromic layers on transparent conductive glass substrates are laminated together with a layer of proton conductor (e.g. poly(2-acrylamido-2-methylpropanesulfonic acid) **PAMPS** or poly(vinylalcohol-phosphoric acid) **PVAP** or a layer of ion conductor, e.g. $LiClO_4$ or CF_3SO_3Li salt in poly(ethylene) oxide-propylene carbonate **PEO** gel, poly(ethylene)imine **PEI** or photocross-linked methoxy poly(ethylene glycol methacrylate)-poly(ethylene glycol diacrylate) **MPEGM-PEGD**. The overall window stucture is shown in Figure 1.

4. ALL-SOLID SMART WINDOW DEVICES

We have successfully prepared protype three-layer, four-layer and five-layer smart window devices [15,16]. Five-layer devices which are in fact an electro-optically active battery, are probably the most useful for relatively large area applications such as windows. Different devices were fabricated and studied:

SnO_2/Poly(BAn)/PAMPS/WO_3/SnO_2	Device I
ITO/Poly(PAn)/PEO/WO_3/ITO	Device II
ITO/Poly(An)/PEI/WO_3-MO_3/ITO	Device III
ITO/Poly(An)/MPEGM-PEGD/WO_3/ITO	Device IV

Their electrochromic properties are illustrated in Figures 2-5. As the applied voltage was varied, the combined colors of the device changed from transparent clear yellow at - 0.1 V to deep blue at 1.0 V.

The electrochemical and optical properties of **Devices I-III** were already presented elsewhere [15,16]. The cyclic voltammogram of **Device IV** is shown in Figure 6. Three redox couples are observed between - 0.5 and 1.5 V, corresponding to the oxidation and reduction of WO_3 and Poly(An) [15]. For Poly(An), the oxidation peaks at 0.4 and 0.9 V are related to the polaron and bipolaron formation. In correlation with these redox peaks, **Device IV** exhibits multiple and reversible color changes from pale yellow at - 0.5 V to deep blue at 1.5 V.

Transmission spectra of **Device IV** at different applied voltages between the bleached state (-0.5 V) and the colored state (+ 1.5 V) are shown in Figure 5. The response time of **Device IV** is quite acceptable when the applied voltage is switched between 1.5 and - 1.5 V (transmittance between 83 and 13 %) as shown in Figure 7. The device was left at room temperature for two days in the bleached state (82 % transmissivity) and in the colored state and the variation in transmissivity was measured. No significant variation is noticed as can be seen in Figure 8.

5. CONCLUSION

In this paper, we have shown some fundamental and practical aspects of complementary five-layer transmissive electrochromic devices. The electrochromic layers are prepared by new large surface deposition techniques (electropolymerization and electrodeposition). Different ionically conductive polymer electrolytes were used in the cell design. The transmittance of the all solid-state devices can be arbitrarily controlled within the range from 80 % to 10 %. Depending on the electrochromic materials used, multicolor and aesthetic electrochromic windows can be fabricated. These results suggest that our devices could be good candidates for electrochromic smart windows.

6. ACKNOWLEDGEMENTS

This work is supported by operating and strategic grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and by contracts from Energy, Mines and Ressources Canada (EMR). We wish to gratefully acknowlegde the enthusiastic support and encouragement of Mr. Tim Mayo, coordinator of Solar Energy Development Program (EMR). L.H.D. is grateful to the invaluable help of graduate students and post-docs whose names appear in the cited references.

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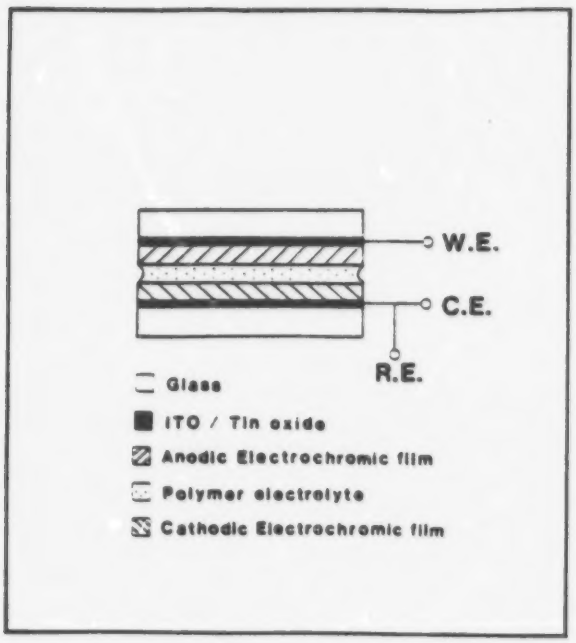

Figure 1. Structure of a complementary electrochromic window

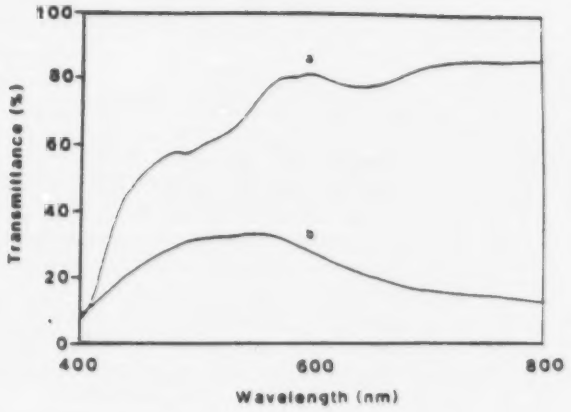

Figure 3. Transmission spectra of device II: a) bleached state, b) colored state

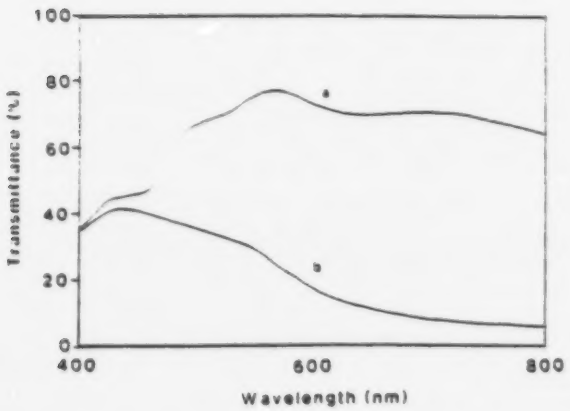

Figure 2. Transmission spectra of device I. a) bleached state, b) colored state

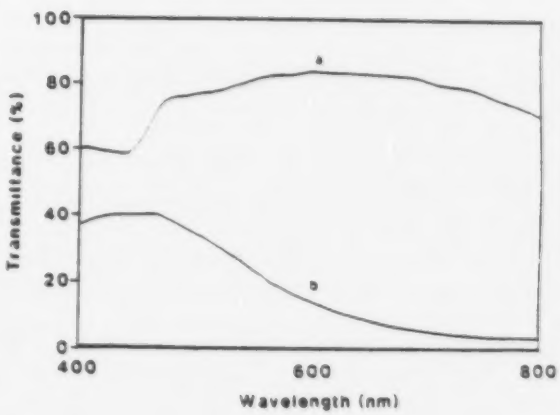

Figure 4. Trnasmission spectra of device III: a) bleached state, b) colored state

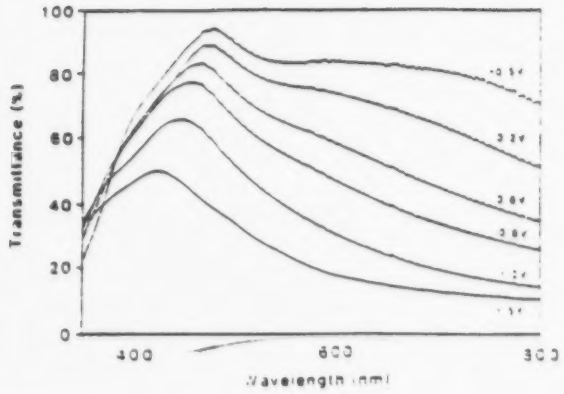

Figure 5. Transmission spectra of device IV at various applied voltages.

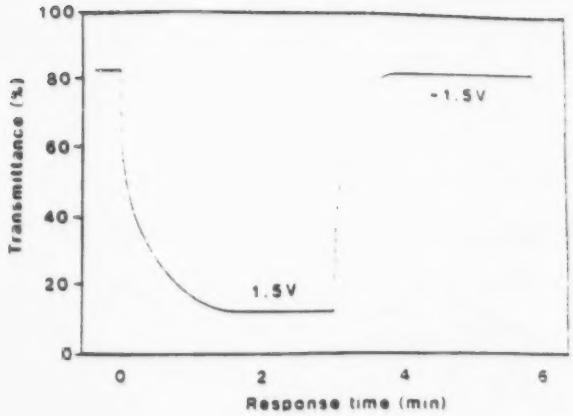

Figure 7. Response time of device IV

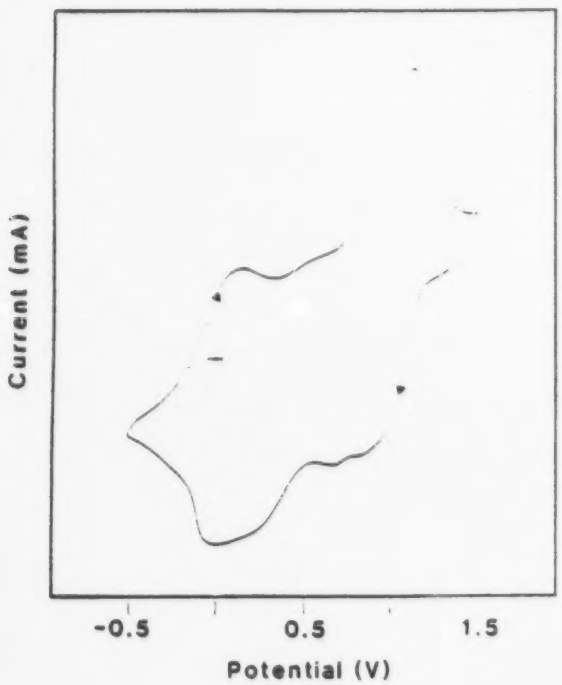

Figure 6. Cyclic voltammogram of device IV at 50 mV/sec

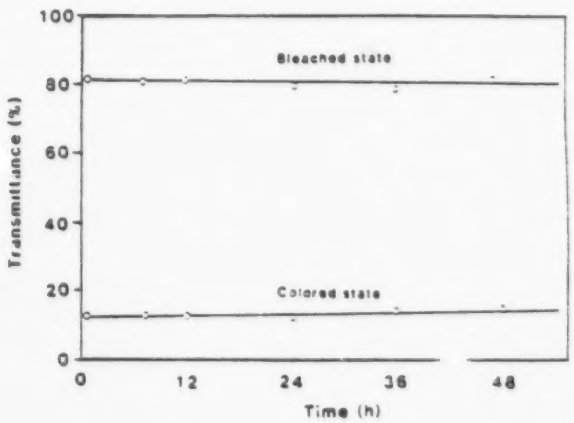

Figure 8. Memory characteristic of device IV

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PROCEEDINGS OF THE SYMPOSIUM ON

ELECTROCHROMIC MATERIALS

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PHYSICAL ELECTROCHEMISTRY DIVISION

Proceedings Volume 90-2

THE ELECTROCHEMICAL SOCIETY, INC., 10 South Main St., Pennington, NJ 08534-2896

PROTOTYPE SOLID-STATE ELECTROCHROMIC WINDOW DEVICES.

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ABSTRACT

Electrochromic smart windows are prospective devices for the control of light transmission in response to the variation of brightness of the environment. The fabrication of electrochromic windows based on cathodically coloring transition metal oxides and anodically coloring conducting polymers are described. The device consists of gel or glassy polymer electrolytes sandwiched by a pair of transparent conducting glass (ITO or Nesa) coated respectively with a thin film of WO_3 or MoO_3 prepared by electrodeposition, and with a thin film of poly(aniline) derivatives obtained by electropolymerization or solution casting. The electrochromic properties of the five-layer smart window devices are presented.

INTRODUCTION

Electrochromic "smart" windows are prospective devices for the control of light transmission in response to the change in brightness of the environment. The basic structure of such a window or electrochromic cell is comprised of three types of thin film materials: a) transparent electrical conductors **TEC** (e.g. ITO, Nesa) on glass or plastic supports to collect the current, b) electrochromic **EC** layer films on **TEC** to form the opto-electroactive elements of the window and c) an ionically conductive electrolyte to separate the two **EC** films (Figure 1).

A large variety of materials are known to display electrochromism. They may be divided into five general classes : a) transition-metal oxides, b) conductive polymers, c) organic, d) intercalated and e) other materials [1]. The bulk of the research published to date have been related to transition-metal oxides (e.g. WO_3, MoO_3, IrO_2 etc.) [1], although many works have been carried out recently on conductive polymers [2,3].

Many electrochromic cells reported in the literature are lacking one or more of the basic components described in Figure 1, resulting in poor long term stability and cyclability. Complementary electrochromic windows, based on cathodically coloring WO_3 and anodically coloring IrO_2 [4] or polyaniline [5], have been fabricated. However, their development is still limited by high costs of fabrication (vacuum evaporation, sputtering), prohibitive costs of materials (IrO_2) and short term stability of materials (polyaniline).

Extended work has been carried out in this laboratory on developing new low cost electrochromic materials and inexpensive large surface thin film deposition techniques for displays and window applications [3, 6-16].

We report here the fabrication and the characterization of some all solid-state prototype electrochromic window devices.

ELECTROCHROMIC SMART WINDOW STRUCTURE

A complementary electrochromic window device is based on a combination of a cathodic electrochromic electrode and an anodic electrochromic electrode separated by a solid electrolyte [15-18]. The operation of the electrochromic device is such that both layers participate in the coloring and bleaching processes, therefore enhancing the overall efficiency of optical switching. For example, the electrochromic reactions occurring in tungsten oxide cathodes and poly(aniline) anodes during optical switching are the following:

$$WO_3 + xM^+ + xe^- \underset{\text{anodic}}{\overset{\text{cathodic}}{\rightleftharpoons}} M_xWO_3$$

transparent — blue

$$\text{Poly(An)} + xA^- - xe^- \underset{\text{cathodic}}{\overset{\text{anodic}}{\rightleftharpoons}} \text{Poly(An)}A_x$$

pale yellow — blue

WO_3 film undergoes a transparent to blue modulation on the electrochemical insertion (coloring) or ejection (bleaching) of a cation M^+, typically H^+, Li^+ or Na^+. In the same time, poly(An) modulates between pale yellow to blue on the electrochemical injection (coloring) or extraction (bleaching) of an anion A^-, typically ClO_4^-, $CF_3SO_3^-$. When the direction of the current flow in the tungsten oxide poly(aniline) electrochromic device is such that the tungsten oxide layer is the cathode and poly(aniline) layer the anode, a dual injection of M^+ in WO_3 and A^- in poly(An) takes place and the electrochromic device develops a deep blue coloration. When the direction of the current flow is reversed, the cation and anion are ejected from the electrochromic layers **EC** to the electrolyte reservoir. The electrochromic device returns then to the transparent state (Figure 2).

Anodic Electrochromic Layer

As reported before [9,10], we have found that electronic conducting polymers films are good candidates for the electrochromic anodic layer. The electrochromic properties of polyaniline films been studied for display devices applications. It has been reported that an electropolymerized polyaniline film showed multiple color changes from transparent yellow at - 0.2 V vs. SCE to green at 0.5, dark blue at 0.8 and black at 1.0 V. Since poly(aniline) deteriorated upon exposure to potentials higher than 0.6 V in acidic aqueous solution, it is necessary to lower the upper potential limit (to 0.4 V, green color) to get durable repetitive cycles but at the expense of color contrast and range. The addition of substituents on poly(aniline) is a general method to modify the properties of the polymers. Polyaniline and diphenylamine derivatives with substituents on the aromatic ring or on the nitrogen were prepared by chemical or electrochemical polymerization (Figure 3). Uniform and stable thin films showing good and stable electrochromic properties were deposited on transparent conducting electrodes directly by electropolymerization or from solution casting. No significant modification in the cyclic voltammograms were observed after thousand cycles in aqueous acid solution or in acetonitrile. Upon cycling between the potential limits (first and second oxidations peaks), most of poly(aniline) derivatives films show multiple and reversible colors changes from pale yellow to dark blue. Among the electrochromic anodic materials, two best candidates -poly(N-phenylaniline) **Poly(PAn)** and poly(N-benzylaniline) **Poly(BAn)**- were selected and used in the prototype smart window devices.

Cathodic Electrochromic Layer

Of the identified candidate materials for the electrochromic cathodic layer, WO_3 is still the primary material since it combines robustness with long-term stability, although recent works seem to indicate that the electrochromic response of MoO_3 is aesthetically superior [13,19]. We have recently

prepared thin films of transition metal oxides and mixtures thereof by electrodeposition [12,13]. The coating cosmetics are excellent and electrochromic property compares favourably to those obtained by other deposition techniques [17].

Ionically Conductive Electrolytes

Solid, gel and glassy polymers were used as ionically conductive electrolytes. The two electrochromic layers on transparent conductive glass substrates are laminated together with a layer of proton conductor (e.g. poly(2-acrylamido-2-methylpropanesulfonic acid) **PAMPS** or poly(vinylalcohol-phosphoric acid) **PVAP**, or a layer of ion conductor, e.g. $LiClO_4$ or CF_3SO_3Li salt in poly(ethylene) oxide-propylene carbonate **PEO** gel, poly(ethylene)imine **PEI** or photocross-linked methoxy poly(ethylene glycol methacrylate)-poly(ethylene glycol diacrylate) **MPEGM-PEGD** elastomers.

ALL-SOLID SMART WINDOW DEVICES

We have successfully prepared prototype three-layer, four-layer and five-layer smart window devices [15,16]. Five-layer devices which are in fact an electro-optically active battery, are probably the most useful for relatively large area applications such as windows. Different devices were fabricated and studied:

SnO_2/Poly(BAn)/PAMPS/WO_3/SnO_2	Prototype I
ITO/Poly(PAn)/PEO/WO_3/ITO	Prototype II
ITO/Poly(PAn)/PEI/WO_3-MO_3/ITO	Prototype III
ITO/Poly(PAn)/MPEGM-PEGD/WO_3/ITO	Prototype IV

The electrochemical and optical properties of prototypes I and IV were already presented elsewhere [15,16].

The cyclic voltammogram of prototype II is shown in Figure 4. For comparison, cyclic voltammograms of WO_3 and Poly(PAn) films on ITO dipped in 1 M $LiClO_4$/propylene carbonate with a Ni counter-electrode are shown in Figures 5 and 6. As observed before [20], only one oxidation peak is observed for WO_3 when the potentials were scanned between - 0.8 and 0.6 V vs. an Ag/AgCl reference electrode (Figure 5). Poly(PAn) film presents two

oxidations peaks at 0.5 and 0.85 V vs. Ag/AgCl (Figure 6). These oxidation peaks are related to the polaron and bipolaron formation [7]. In correlation with these redox processes, WO_3 and poly(PAn) films show multiple and reversible color changes. Visible transmittance spectra of these films doped in 1.0 M $LiClO_4$/PC at different applied voltages are shown in Figures 7 and 8.

Prototype II, contrary to its components, presents no well defined redox peaks (Figure 4) when the applied potentials were scanned between - 0.2 and 1.2 V. However, as the applied voltages were changed, **prototype II** exhibits multiple and reversible color transformation from pale yellow at - 0.2 V to deep blue at 1.2 V. The transmittance spectra of **prototype II** at different applied voltages between the bleached state (- 0.1 V) and the colored state (+ 1.0 V) are shown in Figure 9.

The response time of **prototype II** (60 sec) is quite acceptable for an all solid-state prototype when the applied voltage is switched between + 1.5 and - 1.5 V (transmittance between 83 and 13 %) as shown in Figure 10.

The **prototype II** was left at room temperature for 16 days in the bleached state (62 % transmissivity) and in the colored state (16 %), and the variation in transmissivity was measured. No significant variation in the transmissivity is noticed as can be seen in Figure 11.

Prototype II was also submitted to deep and complete charge and discharge cycles (+/- 1.5 V) and the result is shown in Figure 12. The colored state seems to be more strongly affected than the bleached state, and after 15 thousand cycles, the contrast (colored and bleached states) dropped more than 30%.

The self-discharge curve of **prototype II** is shown in Figure 13. The **prototype II** was charged at 1.0 V and the variation of the transmittance at 700 nm in the open circuit was followed in the time. The electrochromic **prototype** gained about 30% in transmittance after 24 h.

The long term stability and the coloration contrast are strongly influenced by the electrolyte used. In order to improve the characteristic and stability of the window prototype, a new electrolyte based on poly(ethylene imine) was used.

The transmission spectra of **prototype III** at different applied voltages are shown in Figure 14. The **prototype III** changed its color from colorless at - 0.1 V (80 % transmittance) to deep dark blue at 2.0 V (5 % transmittance at 800 nm).

The response times of **prototype III** at room temperature changed from 6 min for an applied voltage of 2.0 V to about 3 min for a higher applied voltage (2.5 V) as shown in Figure 15. Although **prototype III** has a slower switching time compared to **prototype II**, it holds its charge better as shown in Figure 16.

The open circuit voltage decay of **prototype III** charged at 2.0 V shows a far better self-discharge curve (about 20 % of transmittance variation) after 5 days compared to 30 % in 1 day for **prototype II**. In fact, **prototype III** is very stable and no significant change in its properties has been detected after 6 months of cycling testing.

CONCLUSION

We have shown some fundamental and practical aspects of complementary five-layer transmissive electrochromic devices. The electrochromic layers are prepared by new large surface deposition techniques (electropolymerization and electrodeposition). Different ionically conductive polymer electrolytes were used in the cell design. The transmittance of the all solid-state devices can be arbitrarily controlled within the range from 80 % to 10 %. Depending on the electrochromic materials used, multicolor and aesthetic electrochromic windows can be fabricated. These results suggest that our devices could be good candidates for electrochromic smart windows.

ACKNOWLEDGEMENTS

This work is supported by operating and strategic grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and by contracts from Energy, Mines and Resources Canada (EMR). L.H.D. is grateful to the invaluable help of graduate students and post-docs whose names appear in the cited references.

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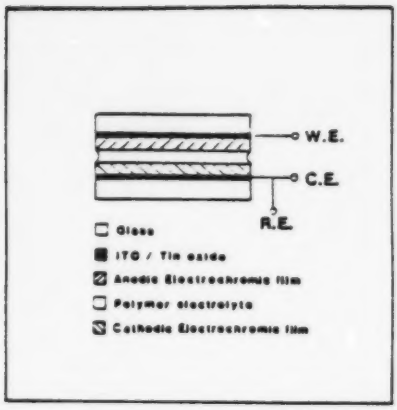

Figure 1. Structure of an electrochromic smart window device.

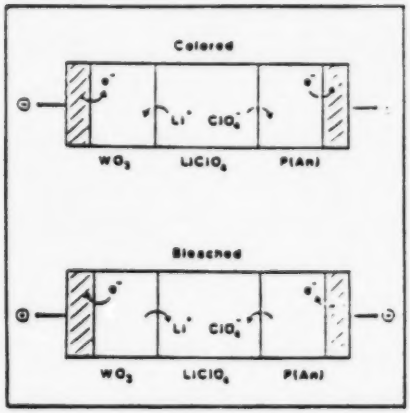

Figure 2. Operation of a complementary electrochromic device

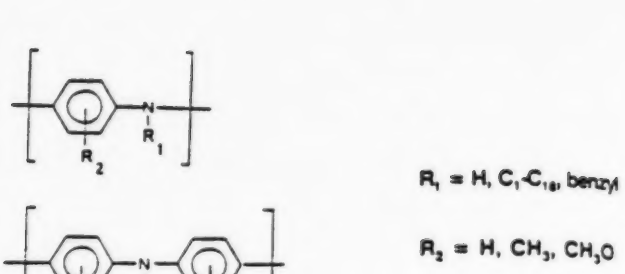

Figure 3. Poly(aniline) and poly(diphenylamine) derivatives

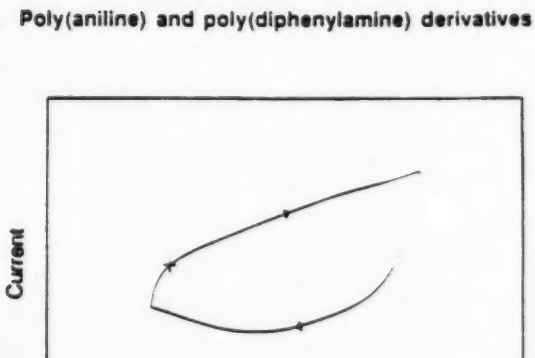

Figure 4. Cyclic votammogram of prototype II (scanning rate: 10 mV/s)

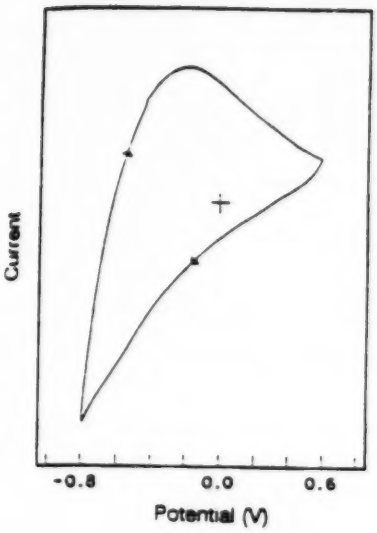

Figure 5. Cyclic voltammogram of WO_3 in 1.0 M $LiClO_4$-PC solution with a Ni counter-electrode (scanning rate: 20 mV/s)

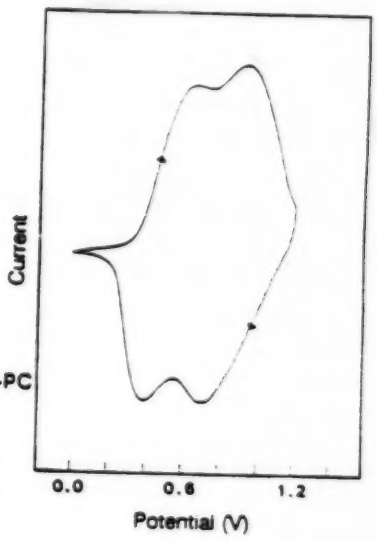

Figure 6. Cyclic voltammogram of poly(DPA) in 1.0 M $LiClO_4$-PC solution with a Ni counter-electrode (scanning rate: 20 mV/s) .

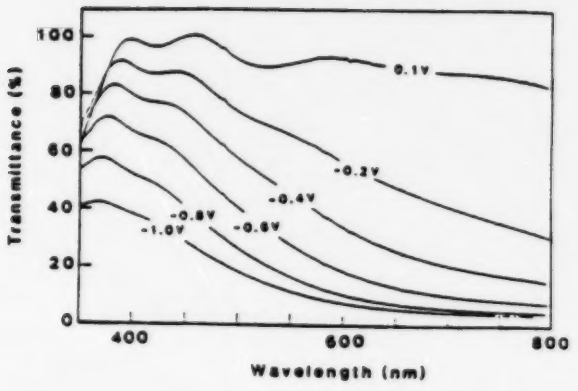

Figure 7. Transmittance spectra of WO_3 in 1.0 M $LiClO_4$-PC solution with a Ni counter-electrode.

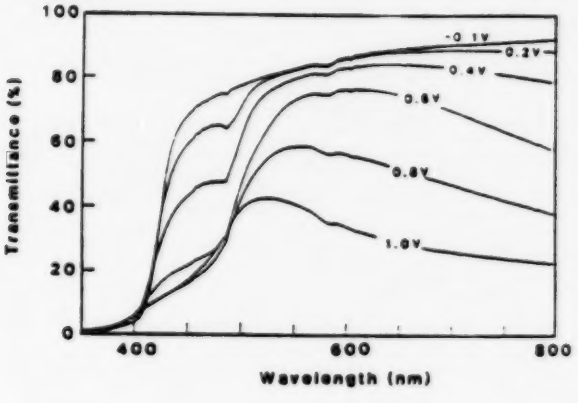

Figure 8. Transmittance spectra of poly(DPA) in 1.0 M $LiClO_4$-PC solution with a Ni counter-electrode.

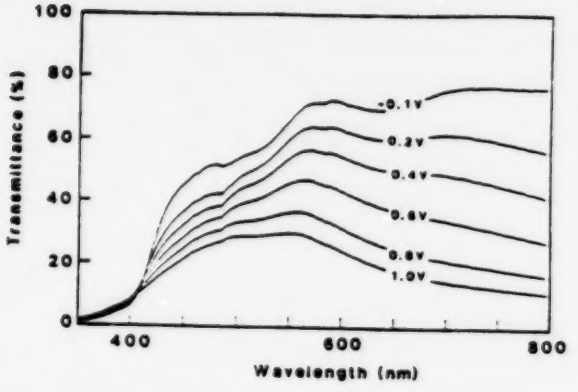

Figure 9. Transmittance spectra of prototype II at different applied voltages.

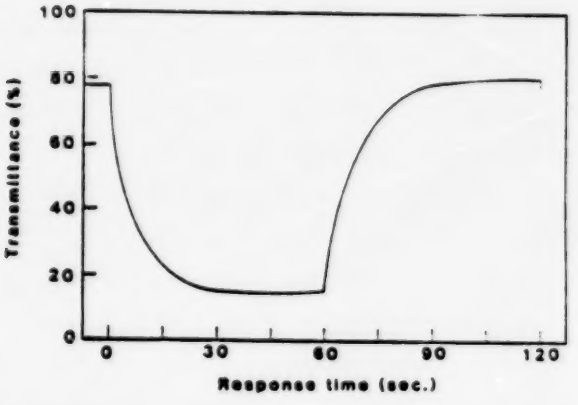

Figure 10. Switching response of prototype II at +/- 1.5 V applied voltages.

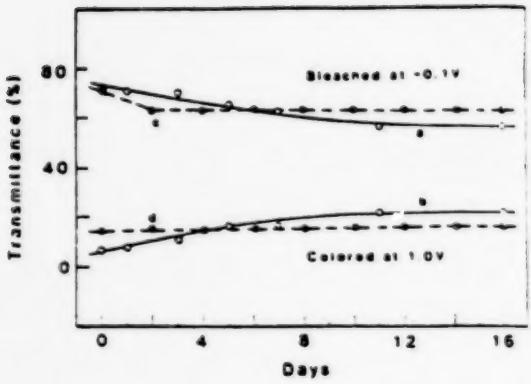

Figure 11. Transmittance in the bleached and colored states for device I (curves a and b) and device II (curves c and d)

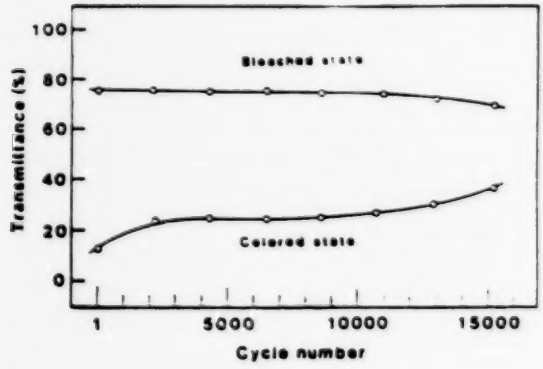

Figure 12. Transmittance in the bleached and colored states of prototype II as a function of cycle number.

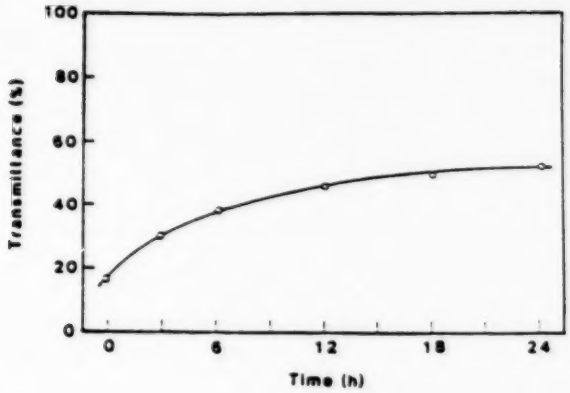

Figure 13. **Self-discharge of prototype II.**

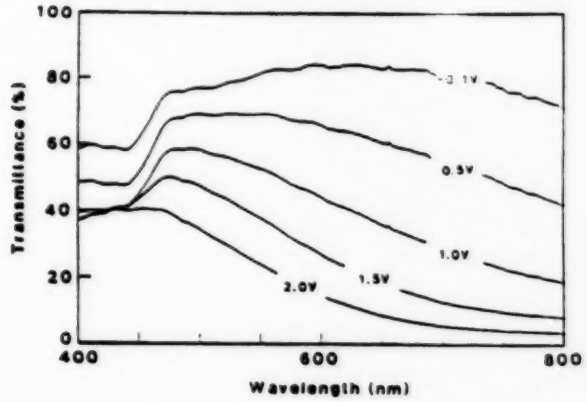

Figure 14. **Transmittance spectra of prototype II at different applied voltages.**

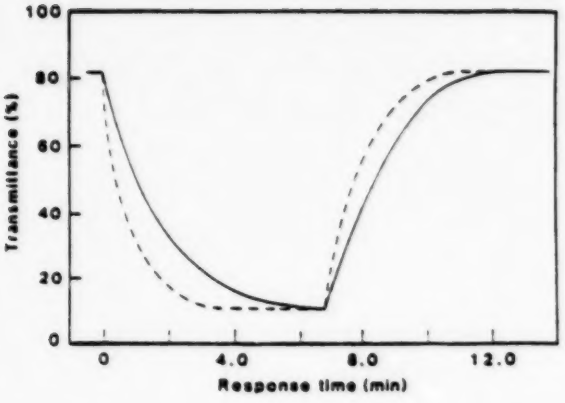

Figure 15. Switching response of prototype III at applied voltage of +/- 2.0 V and +/- 2.5 V.

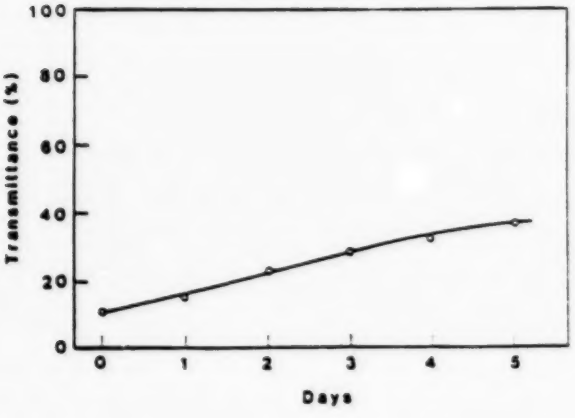

Figure 16. Self-discharge of prototype III.